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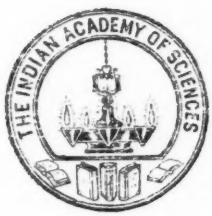

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*ON SYMMETRIC FUNCTIONS OF m SYMMETRIC FUNCTIONS IN A BOOLEAN ALGEBRA

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Received December 9, 1938
(Communicated by Dr. R. Vaidyanathaswamy)

It is well known that a Boolean Algebra generated from n elements $[A_1, A_2, \cdots, A_n]$ (which may be considered as sub-classes of a certain class I, called the Universe) possesses a set of elements called *Minimal-Elements* with the following properties[1] (1) The product of two distinct minimals is zero ; (2) The sum of all the minimals is I; (3) Any element of $[A_1, A_2, \cdots, A_n]$ can be expressed uniquely as a sum of these minimals. It[2] is also well known that the Boolean Algebra $[A_1, A_2, \cdots, A_n]$ is isomorphic with the algebra of all sub-classes of the class constituted by the minimal-elements of the Boolean Algebra.

If now we form all the symmetric functions p from the n elements A by the three primary Boolean operations[3] $+$, $\times$ and negation as well as the secondary operations disjunction ($\oplus$) and conjunction ($\otimes$), it is clear that the sums and products as well as the negatives of the symmetric functions p are also symmetric functions and hence it follows[4] that the algebra $\{A_1, A_2, \cdots, A_n\}$ of all the symmetric functions p is a sub-algebra of the Boolean Algebra $[A_1, A_2, \cdots, A_n]$. Therefore in accordance with the theorem of the

*This paper which was read at the Fourth Conference of the Indian Academy of Sciences, held in Madras, is a revised and condensed form of part of a thesis for which the degree of M.Sc. was recently awarded by the University of Madras. I take this opportunity to thank Dr. Vaidyanathaswamy for his kind guidance and encouragement during the preparation of this paper.

[1] For proofs of these well-known properties see my papers : " On Finite Boolean Algebra " (Sec. II, theorem 12) to appear shortly in the *Mathematics Student* and " On Symmetric Functions of n Elements in a Boolean Algebra," *Jour. Indian Math. Soc.*, 2, No. 5, 200. For the sake of brevity, these two papers will hereafter be referred to as *Paper* 1, *Paper* 2.

[2] A proof of this fundamental theorem is given in *Paper* 1.

[3] The nomenclature here is the same as in *Paper* 2, pp. 198–210.

[4] See *Paper* 2, p. 201.

Boolean Algebra (stated above) this sub-algebra should be isomorphic with the algebra of *all* sub-classes of the class constituted by the minimal-elements of this algebra. These minimals have been shown in the abovementioned paper[5] to be a certain kind of functions called the β-functions (where β_r, $r = 0, 1, \cdots, n$ is defined as the class of elements belonging to exactly r of the classes A) such that (1) the product of two distinct β's is zero. (2) The sum of all the β's is I (the Universe). (3) Any symmetric function p can be uniquely expressed as the sum of β's. The symmetric function p is then said to be expressed in the ' normal form ' or the ' canonical form '.

I. The General Symmetric Function P $(p_1, p_2, \cdots, p_m)$

Let us now consider m assigned symmetric functions $p_1, p_2, \cdots, p_m$ of $A_1, A_2, \cdots, A_n$. Then it is clear that the algebra $\{p_1, p_2, \cdots, p_m\}$ of all the symmetric functions P of $p_1, \cdots, p_m$ is a sub-algebra of $\{A_1, A_2, \cdots, A_n\}$,— for, the P's being symmetric functions of the p's, are naturally symmetric functions of the A's. Therefore, the P's can be expressed in the canonical form (*i.e.*, as sums of β's). The object of this paper is to give a general method of expressing any known symmetric function P $(p_1, p_2, \cdots, p_m)$ in its canonical form and evaluate P in special cases.

Denoting the minimal-elements of $\{p_1, p_2, \cdots, p_m\}$ by $B_0, B_1, \cdots, B_m$, it is clear from general reasoning that B_i, $i = 0, 1, \cdots, m$ is the class of elements which occur in exactly i of the classes p. Hence, any symmetric function P $(p_1, p_2, \cdots, p_m)$ of $\{p_1, p_2, \cdots, p_m\}$ can be uniquely expressed as a sum of B's. And from the fact that $\{p_1, p_2, \cdots, p_m\}$ is a sub-algebra of $\{A_1, A_2, \cdots, A_n\}$ these B's are the sums of the β's. Hence, the problem of expressing P $(p_1, p_2, \cdots, p_m)$ in its canonical form will be solved if we know how to express B's in terms of β's. This is capable of direct solution. For, we have seen that B_i is the class of elements which occur in exactly i of the classes $p_1, p_2, \cdots, p_m$. But we know that $p_1, p_2, \cdots, p_m$ being symmetric functions of $A_1, A_2, \cdots, A_n$ can be expressed in their canonical forms (as sums of the mutually exclusive classes $\beta_0, \beta_1, \cdots, \beta_n$ into which the Universe I has been split up). Therefore, if a certain element occurs in i of the classes $p_1, p_2, \cdots, p_m$ it means that the particulars β of which that element is a member occurs in those i classes. That is to say, the class B_i of those elements which occur in i of $p_1, p_2, \cdots, p_m$ is the sum of the classes β_j which occur as sub-classes of exactly i of the classes $p_1, p_2, \cdots, p_m$. Or symbolically, $B_i = \Sigma\, \beta_j$ *summed for* j such *that* $t_j = i$ *where* t_j *is the number of* p's *in the normal forms of which* β_j *occurs.*

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[5] See *Paper* 2, pp. 201, 202.

This leads to a direct calculation of the B's in terms of β's and hence to the evaluation of P $(p_1, p_2, \cdots, p_m)$ in its canonical form.

II. The Double-Symmetric Functions

Dr. Vaidyanathaswamy[6] in an investigation of the Arithmetico-Logical Symmetric Functions of n Attributes, defined a particular kind of symmetric functions α_k (which he called logico-symmetric functions) as the logical sum of the logical products k at a time of the n elements $A_1, A_2, \cdots, A_n$. These functions α can be conveniently indicated by the notation

$$\alpha_k (A_1, \cdots, \cdots, A_n) = S_k (\times, +; A_1, A_2, \cdots, A_n),\ k = 1, 2, \cdots, n.$$

It is clear that if instead of $\times$, $+$ we substitute any two of the four boolean operations $+$, $\times$, $\oplus$, $\otimes$, we can form 4 $P_2 = 12$ distinct symmetric functions of this type. These twelve symmetric functions which have been expressed in the normal form in my previous paper,[7] I call the standard type and denote them in general by $S_k (u_1, v_1; A_1, \cdots, A_n)$ where $k = 1, 2, \cdots, n$ and u_1, v_1 any two of the four fundamental boolean operations $+$, $\times$, $\oplus$, $\otimes$.

We shall consider here, a particular case of P $(p_1, p_2, \cdots p_m)$ where (1) $m = n$; (2) $p_k = S_k (u_1, v_1; A_1, A_2, \cdots, A_n)$, $k = 1, \cdots, n$; (3) P $(p_1, p_2, \cdots, p_m)$ $= S_r (u, v)$ $(p_1, p_2, \cdots, p_m) = S_r (u, v)$ S $(u_1, v_1; A_1, \cdots, A_n)$ where again u, v are chosen as any two of the four boolean operations $+$, $\times$, $\oplus$, $\oplus$. These symmetric functions of the symmetric functions $S(u_1, v_1; A_1, A_2, \cdots, A_n)$, I call *Double-Symmetric Functions.* S $(u_1, v_1; A_1, \cdots, A_n)$ may be termed the 'inner function' while S (u, v) can be called the 'outer function' of the double-symmetric function $S_r (u, v)$ S $(u_1, v_1; A_1, A_2, \cdots, A_n)$. It is clear there are $12 \times 12 = 144$ double-symmetric functions of this type; for there are twelve sets, every set having the same outer function for a set of twelve inner functions or *vice versa.*

It is interesting to notice that the values of these double-symmetric functions are not *all* distinct but by the general principle of duality[8] can be reduced to the following thirty-six,—namely the double-symmetric functions whose inner and outer functions are chosen from the following types of symmetric functions of n arguments,

$$S (\times, +), S (\times, \oplus), S (\oplus, \times), S (+, \oplus), S (\oplus, +), S (\oplus, \otimes).$$

Of these cases, the six double-symmetric functions whose inner functions are

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[6] R. Vaidyanathaswamy, "On the Arithmetico-Logical Symmetric Functions of n Attributes," *Proc. Ind. Acad. Sci.*, 1935, **2**, 56.

[7] *Paper* 2, p. 205.

[8] For detailed information, see *Paper* 2, p. 204.

$S_k (\times, +; A_1, \cdots, A_n)$ $k = 1, \cdots, n$, are trivial and may be omitted. For, as shown in a previous paper,[9]

$$S_k (u_1, v_1; a_1, a_2, \cdots, a_n) = S_k (u_1, v_1; A_1, A_2, \cdots, A_n) = \Sigma \beta_i.$$

III. The Double-Symmetric Functions with S $(\oplus, \times)$, S $(\oplus, +)$ *as Inner Functions*

We shall now evaluate in the canonical form, by the general method indicated already some interesting double-symmetric functions chosen from the above. Taking up first the six double-symmetric functions whose inner functions are $S_k (\oplus, \times; A_1, \cdots, A_n)$ $k = 1, 2, \cdots, n$, the inner functions in this case are, from the general formulæ[10]

$$\begin{aligned} p_{2k+1} &= S_{2k+1} (\oplus, \times; A_1, \cdots, A_n) = \beta_n \quad (2k + 1 < n) \\ p_{2k} &= S_{2k} \quad (\oplus, \times; A_1, \cdots, A_n) = 0 \quad (2k < n) \\ p_n &= S_n \quad (\oplus, \times; A_1, \cdots, A_n) = \text{Sum of odd } \beta\text{'s.} \end{aligned}$$

By simple inspection, t_j which [by (i) of sec. I] is the number of S's in the normal forms of which β_j occurs, is seen to be

$\underline{\mathrm{I}\left(\frac{n+1}{2}\right)}$ for $j = n$ and n odd or even,

$\underline{1}$ for $j \neq n$ and j odd,

$\underline{O}$ for $j \neq n$ and j even.

$\left[\text{If } n = 2, \text{ we get } \mathrm{I}\left(\frac{n+1}{2}\right) = 1. \quad \text{Hence we assume } n > 2\right)\Big]$.

The corresponding B's [since from sec. I (i) $B_i = \Sigma \beta_j$ summed for j such that $t_j = i$) are then found to be

$$B_{\mathrm{I}\left(\frac{n+1}{2}\right)} = \beta_n.$$

$$\left.\begin{aligned} B_1 &= \beta_1 + \beta_3 + \cdots \\ B_0 &= \beta_0 + \beta_2 + \cdots \end{aligned}\right\} \text{ excluding } \beta_n.$$

$$B_i = O \text{ for all other values of } i.$$

We can now easily calculate the six double-symmetric functions whose inner functions are $S_k (\oplus, \times; A_1, A_2, \cdots, A_n)$, $k = 1, \cdots, n$.

As an illustration we consider $S_r (\oplus, \times)$ S $(\oplus, \times; A_1, A_2, \cdots, A_n)$.

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[9] *Paper* 2, Theorem IV.

[10] *Ibid.*, p. 205.

From the general formulæ[11] [since B's are minimals of $\{p_1, p_2, \cdots, p_m\}$], we have

$$S_r(\oplus, \times)\, S(\oplus, \times; A_1, A_2, \cdots, A_n) = \begin{cases} O \text{ when } r \text{ is even } (r \neq n). \\ B_n \text{ when } r \text{ is odd } (r \neq n). \\ \text{Sum of odd B's } (r = n). \end{cases}$$

Hence substituting for B, we obtain

when $r \neq n$,

$S_r(\oplus, \times)\, S(\oplus, \times; A_1, A_2, \cdots, A_n) = O$ for r odd or even.

$\left[\text{Since } n > I\left(\frac{n+1}{2}\right) \text{ for } n > 1\right]$.

But if r is odd and $n = 1$, then $I\left(\frac{n+1}{2}\right) = 1$ in which case,

$S_r(\oplus, \times)\, S(\oplus, \times; A_1, A_2, \cdots, A_n) = \beta_n$.

when $r = n$,

$S_n(\oplus, \times)\, S(\oplus, \times; A_1, A_2, \cdots A_n) = B_1$ *or* $B_1 + B_I\left(\frac{n+1}{2}\right)$

according as $I\left(\frac{n+1}{2}\right)$ is even or odd (*i.e.*, according as $n = 4k$, $4k+3$ *or* $4k+1$, $4k+2$).

Now substituting for B's in terms of β's, we get

$S_n(\oplus, \times)\, S(\oplus, \times; A_1, A_2, \cdots, A_n) = \beta_1 + \beta_3 + \cdots$ (exc'uding β_n) *or* $=$ $(\beta_1 + \beta_3 + \cdots) + \beta_n$ in the respective cases.

Exactly the same method can be followed to evaluate the other five double-symmetric functions with the inner functions $S_k(\oplus, \times; A_1, A_2, \cdots, A_n)$, $k = 1, \cdots, n$, as also the six double-symmetric functions whose inner functions are $S_k(\oplus, +; A_1, \cdots, A_n)$, $k = 1, \cdots, n$.

IV. The Double-Symmetric Functions with S $(\times, \oplus)$ *as Inner-Functions*

We next consider a different type of double-symmetric functions where the t_j's cannot be written down by simple inspection ; the evaluations in these cases are reduced to the solutions of certain combinatorial arithmetical problems which are not explicitly solvable in all the instances. For example, let us consider the six double-symmetric functions whose inner functions are $S_k(\times, \oplus; A_1, A_2, \cdots, A_n)$, $k = 1, \cdots, n$.

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[11] *Paper* 2, p. 205.

As before from the general formulæ,[12] the inner functions p are $S_k(\times, \oplus; A_1, A_2, \cdots, A_n) = \Sigma \beta_i$ summed for i such that $\binom{t}{k}$ is odd and $k = 1, \cdots, n$.

And t_j [which from (i) of sec. I is the number of S's in the normal forms of which β_j occurs] = the number of values of k for which $\binom{i}{k}$ is odd.

To obtain t_j explicitly, we require the following lemma

LEMMA 1. *If i is any integer,*

(*a*) *The numbers* k *for which* $\binom{t}{k}$ *is odd, are those which are obtained by replacing any number of the units in the expression of i in the binary scale by zero's.*

(*b*) *The number of values of* k *for which* $\binom{i}{k}$ *is odd is given by* $f(i) = 2^{\sigma(i)}$ *where* σ (i) *is the number of units in the expression of i in the binary scale.*

Proof. Expressing i in the binary scale,

$i = 2^{m_1} + 2^{m_2} + 2^{m_3} + \cdots$ to $\sigma(i)$ terms). $\quad (m_1 > m_2 > m_3 > \cdots)$.

Since $(1 + x)^2 = 1 + x^2$, (mod. 2), it follows by induction,

$$(1 + x)^{2^t} = 1 + x^{2^t}, \text{ (mod 2)} \cdots\cdots\cdots\cdots \text{(i)}$$

Hence,

$$\Sigma \binom{t}{k} x^k = (1 + x)^i = (1 + x)^{2^{m_1}} \cdot (1 + x)^{2^{m_2}} \cdot (1 + x)^{2^{m_3}} \cdots \text{ to } \sigma(i) \text{ terms.}$$

$$= 1 + \Sigma x^{2^{m_1}} + \Sigma x^{2^{m_1} + 2^{m_2}} + \Sigma x^{2^{m_1} + 2^{m_2} + 2^{m_3}} + \cdots \text{ (ii) mod 2.}$$

[from (i) and by simple expansion].

(*a*) It is obvious that the values of k for which $\binom{i}{k}$ are odd, are the indices of x which occur in (ii). These indices are numbers of the form $2^{m_j} + 2^{m_k} + \cdots$, *i.e.*, the numbers which are obtained by replacing any number of units by zeros in the expression of i in the binary scale.

(*b*) The total number of numbers k (including zero) for which $\binom{t}{k}$ is odd, is evidently $2^{\sigma(i)}$ where $\sigma(i)$ is the number of units in the expression of i in the binary scale.

Corollary. If i is of the form $2^t - 1$, then $\sigma(i) = t$. Hence $\binom{i}{k}$ is odd for every $k \leqslant i$.

We thus get t_j (= the number of values of k, excluding zero for which $\binom{i}{k}$ is odd) $= 2^{\sigma(j)} - 1$ where $\sigma(j)$ is the number of units in the expression of i in the binary scale.

The six double-symmetric functions whose inner functions are $S_k(\times, \oplus; A_1, A_2, \cdots, A_n)$, $k = 1, \cdots, n$, can now be evaluated.

We shall take up one example, namely, $S_r(\times, \oplus)\, S(\times, \oplus; A_1, A_2, \cdots A_n)$.

[12] *Paper* 2, p. 205.

As before from the general formulæ[13] we get

$S_r(\times, \oplus)\ S(\times, \oplus; A_1, A_2, \cdots, A_n) = \Sigma B_i$ summed for i such that $\binom{i}{r}$ is odd.

Expressing B_i in terms of β_j as before,

$S_r(\times, \oplus)\ S(\times, \oplus; A_1, A_2, \cdots, A_n) = \Sigma \beta_j$, summed for j such that $\binom{i}{j}$ is odd; *i.e.*, such that $\binom{2^{\sigma(j)} - 1}{r}$ is odd.

When $r = 1$, this result leads to an identity of Bernstein's.[14]

For, $\binom{2^{\sigma(j)} - 1}{1} = 2^{\sigma(j)} - 1$ is always odd for $j > 0$.

Hence,

$$S_1(\times, \oplus)\ S(\times, \oplus; A_1, A_2, \cdots, A_n) = \beta_1 + \beta_2 + \cdots \beta_n = \alpha_1 = A_1 + A_2 + \cdots + A_n.$$

i.e.,

$$\Sigma A_1 \oplus \Sigma A_1 \cdot A_2 \oplus \Sigma A_1 \cdot A_2 \cdot A_3 \oplus \cdots \oplus A_1 \cdot A_2 \cdots A_n = A_1 + A_2 + A_3 + \cdots + A_n.$$

which is Bernstein's identity.

The above identity can be easily generalised for any r.

For, by the corollary of Lemma 1, $\binom{2^{\sigma(j)} - 1}{r}$ is odd for $2^{\sigma(j)} - 1 \geqslant r$.

Hence, $S_r(\times, \oplus)\ S(\times, \oplus; A_1, \cdots, A_n) = \Sigma \beta_i$ summed for i such that $2^{\sigma(i)} - 1 \geqslant r$.

This evaluates $S_r(\times, \oplus)\ S(\times, \oplus; A_1, A_2, \cdots, A_n)$ for any $r > 1$.

V. *The Double-Symmetric Functions with* S (+, ⊕), S (⊕, ⊗) *as Inner Functions*

To calculate t_j when the inner functions are $S_k(+, \oplus; A_1, A_2, \cdots, A_n)$, $k = 1, \cdots, n$, we have to find the number of numbers k for which $\binom{n}{k} - \binom{n-i}{k}$ is odd.[13] It is difficult to deal with this case in general, but however for numerical cases, we can obtain t_j by means of a lemma easily deduced from lemma 1, and which may be briefly stated as follows:

LEMMA 2. *If in the expressions of* i_1, i_2 *and* k (*a variable*) *in the binary scale,* λ_{00}, λ_{11}, λ_{10}, λ_{01} *denote the sets of places in which there are zeros of both* i_1 *and* i_2, *units of both* i_1 *and* i_2 *units of* i_1 *against zeros of* i_2, *zeros of* i_1, *against*

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[13] *Paper* 2, p. 205.

[14] Bernstein, B. A., "Postulates for the Boolean Algebra involving the Operation of Complete Disjunction," *Annals. of Maths.*, 1936 (April), Theorem 30.

units of i_2 respectively, then $\binom{i_1}{k}$ will be odd and $\binom{i_2}{k}$ will be even if k has zeros at λ_{00}, λ_{01}, and has at least one unit in the set of places λ_{10}; $\binom{i_1}{k}$ will be even and $\binom{i_2}{k}$ will be odd if k has zeros at λ_{00}, λ_{10} and one unit at least in the set of places λ_{01}.

It is evident that for $\binom{n}{k} - \binom{n-i}{k}$ to be odd, one of $\binom{n}{k}, \binom{n-i}{k}$ must be odd and the other even. Hence we can at once obtain t_j by expressing $n - i$ in the binary scale and then applying lemma 2, and thus evaluate the six double-symmetric functions whose inner functions are S_k $(+, \oplus ; A_1, \cdots, A_n)$, $k = 1, 2, \cdots, n$.

Lastly, when the inner functions are S_k $(\oplus, \otimes ; A_1, A_2, \cdots, A_n)$, $k = 1, \cdots, n$ to evaluate t_j, we have to obtain the number of numbers k for which the series[13] $\binom{n-i}{k} + \binom{n-i}{k-2}\binom{i}{2} + \binom{n-i}{k-4}\binom{i}{4} + \cdots$ is even. Due to the complicated nature of this series, an explicit evaluation of t_j is not possible except for a few trivial cases of k.

ON A PROBLEM OF ARRANGEMENTS

By Gul Abdulla and Lal Bahadur

Received January 23, 1939

(Communicated by Dr. S. Chowla)

The following problem is still unsolved except in special cases :—

$2n + 1$ people are invited out to dinner on n different days. Is it possible to arrange them on a circular table in such a way that no person has the same neighbour on different days ?

It is easy to show that if $2n + 1 =$ a prime p, then the answer is in the affirmative. For let $(1, 2, 3, \cdots, m)$ denote the arrangement in the counter-clockwise direction of the numbers $1, 2, 3, \cdots, m$ (in this order) round a circle. Then the $\frac{p-1}{2}$ arrangements $\{1, 1 + s, 1 + 2s, 1 + 3s, \cdots, 1 + (p-1)s\}$, where s is given all values from 1 to $\frac{p-1}{2}$, and all numbers greater than p are represented by their least positive residues (mod p), are a solution of our problem.

The case when $(2n + 1)$ is composite, is still unsolved except in special cases. We give here the solution for[1] $n = 10$; also the solution for $n = 4$.

I. $n = 10$. The 10 arrangements are as follows :

(i) {1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 20, 18, 16, 14, 12, 10, 8, 6, 4, 2}
(ii) {1, 4, 7, 10, 13, 16, 19, 2, 21, 18, 15, 12, 9, 6, 3, 20, 17, 14, 11, 8, 5}
(iii) {1, 6, 11, 16, 21, 3, 8, 13, 18, 2, 7, 12, 17, 4, 9, 14, 19, 5, 10, 15, 20}
(iv) {1, 7, 13, 19, 3, 9, 15, 21, 4, 10, 16, 17, 11, 5, 20, 14, 8, 2, 6, 12, 18}
(v) {1, 8, 15, 3, 10, 17, 6, 13, 20, 4, 11, 18, 14, 21, 7, 16, 9, 2, 5, 12, 19}
(vi) {1, 9, 17, 2, 10, 18, 3, 11, 19, 6, 14, 15, 16, 8, 7, 20, 12, 4, 5, 13, 21}
(vii) {1, 10, 19, 4, 13, 14, 5, 6, 15, 2, 16, 20, 9, 18, 7, 11, 21, 8, 12, 3, 17}
(viii) {1, 11, 20, 2, 12, 13, 3, 4, 14, 7, 17, 5, 15, 19, 18, 8, 9, 21, 10, 6, 16}
(ix) {1, 12, 21, 5, 16, 3, 14, 2, 11, 10, 9, 13, 17, 18, 6, 7, 19, 20, 8, 4, 15}
(x) {1, 13, 2, 3, 7, 15, 11, 12, 16, 4, 18, 5, 9, 19, 8, 17, 21, 6, 20, 10, 14}

II. $n = 4$:

(i) {1, 2, 3, 4, 5, 6, 7, 8, 9}
(ii) {1, 3, 5, 7, 9, 2, 4, 6, 8}
(iii) {1, 4, 7, 2, 5, 8, 3, 9, 6}
(iv) {1, 5, 9, 4, 8, 2, 6, 3, 7}

[1] Our attention was drawn to this case by Dr. T. Vijayaraghavan.

A NEW SOLUTION OF THE 10–21 PROBLEM

By S. Chowla

(Government College, Lahore)

Received January 30, 1939

The problem[1] is to arrange the numbers 1, 2, 3, · · ·, 21 in a circle in 10 ways, so that no number has the same neighbours in different arrangements.

Let (1, 2, 3, · · ·, m) denote the arrangement of the numbers 1, 2, 3, · · ·, m in a circle, so that 1 has 2 and m as neighbours, 2 has 1 and 3 as neighbours, etc.

The 10 arrangements are as follows :—

(i) (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21)

(ii) (2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21)

(iii) (4, 8, 12, 16, 20, 3, 7, 11, 15, 19, 2, 6, 10, 14, 18, 1, 5, 9, 13, 17, 21)

(iv) (5, 10, 15, 20, 4, 9, 14, 19, 3, 8, 13, 18, 2, 7, 12, 17, 1, 6, 11, 16, 21)

(v) (10, 20, 9, 19, 8, 18, 7, 17, 6, 16, 5, 15, 4, 14, 3, 13, 2, 12, 1, 11, 21)

(vi) (1, 9, 17, 4, 12, 20, 7, 14, 6, 19, 11, 3, 16, 8, 21, 13, 5, 18, 10, 2, 15)

(vii) (1, 4, 7, 10, 13, 20, 17, 14, 11, 8, 5, 2, 9, 6, 3, 21, 18, 15, 12, 19, 16)

(viii) (13, 7, 1, 19, 5, 20, 14, 8, 2, 11, 17, 3, 9, 15, 21, 6, 12, 18, 4, 10, 16)

(ix) (1, 10, 19, 7, 16, 4, 13, 6, 15, 3, 12, 21, 9, 18, 11, 20, 2, 14, 5, 17, 8)

(x) (1, 13, 19, 4, 11, 5, 12, 9, 16, 2, 17, 10, 3, 18, 6, 20, 8, 15, 7, 21, 14)

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[1] The solution given here is simpler than that of Gul Abdulla and Lal Bahadur, *Proc. Indian Acad. Sci.*, (A), 1939, **9**, 103. As far as the auhor can see the above solution is not a *permutation* of their solution !!

THE RAMAN SPECTRA OF LIQUID SOLUTIONS*

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The additivity of the Raman spectra in liquid mixtures has been often investigated. In some cases, deviations have been found from additivity, as manifested in shifts of the frequencies, in changes of the width of lines and of the ratio of their intensities, and also in the appearance of new frequencies.

These changes have been attributed to a deformation-effect, solvatation, formation of complexes, and so on. In other cases, complete additivity has been observed. Hitherto, no general relations have been found between the deviations from additivity, and the properties of the mixture components.

We have studied in several investigations arsenic, antimony and phosphorus trichlorides in admixture with polar and non-polar solvents. The results of these are the following :—

1. The frequencies of arsenic trichloride in benzene and carbon tetrachloride are almost not shifted. In methyl ethyl, and iso-propyl alcohols, the frequencies 159 and 195 cm.$^{-1}$ remain almost unchanged, but the frequencies 372 and 410 cm.$^{-1}$ are greatly diminished in all the three alcohols (Table I). The frequencies of the alcohols and of CCl_4 and C_6H_6 are not

Table I

The Frequencies of $AsCl_3$ in Mixtures

	Pure	in C_6H_6	in CCl_4	in CH_3OH	in C_2H_5OH	in C_3H_7OH
I	159	153	153	154	159	161
II	195	191	187	198	198	194
III	372	369	382	348	342	344
IV	410	401	408	389	388	378

* Paper intended for publication in the *Raman Jubilee Number*, but received too late.

changed. In each case, we investigated mixtures with 25 to 45 per cent. of arsenic trichloride. Within these concentration limits, there was observed no marked influence of the concentration on the shifts.[1]

2. The solutions of antimony trichloride in methyl and ethyl alcohols (40–50 per cent. $SbCl_3$) show a similar behaviour. The frequencies of the alcohols and the lines at 132 and 160 cm.$^{-1}$ of $SbCl_3$ do not change, but the frequencies 321 and 360 cm.$^{-1}$ of $SbCl_3$ are both lowered down to 302 and 346 cm.$^{-1}$ (Table II). The last two frequencies are raised in carbon disulphide by 20 and 10 cm.$^{-1}$ respectively, but this measurement is doubtful on account of the rapid photolysis of the solution.[1†]

TABLE II

The Frequencies of $SbCl_3$ in Mixtures

	Pure	in CH_3OH	in C_2H_5OH
I	132	129	131
II	160	155	153
III	321	302	302
IV	360	344	348

3. The solutions of phosphorus trichloride in chloroform, carbon disulphide and ethyl ether show complete additivity of the Raman spectra. The intensity ratio for 189, 259, 486 and 511 cm.$^{-1}$ is 100 : 63 : 46 : 73.[3] These data considerably differ from the earlier results of Daure.[4]

The lowering of the intensities with dilution in chloroform solutions is abnormal, though the intensity ratio of the anti-stokes to stokes frequencies ($i_{\text{à}}$ i_{s}) for pure PCl_3 is in good agreement with the theories (Table III). The intensities of the frequencies 189 and 511 cm.$^{-1}$ show both the same lowering from 100 to 72 and 48, if the concentration of the solution in respect of PCl_3 is varied from 100 to 50 and 25 per cent. respectively.

4. The solutions of aluminium chloride in water show no Raman frequencies except water bands,[5] in agreement with the findings of Daure[6] and of Venkateswaran,[7] but in contradiction to that of Hibben.[8]

† M. Ashkinasi and P. Kurnosova in their investigation, carried in our Institute, discovered in the solution of antimony trichloride in benzene two new frequencies 477 and 1236 cm.$^{-1}$. The authors attributed this observation to the formation of a complex $2\,SbCl_3 \cdot C_6H_6$. In ethyl ether the frequencies of antimony trichloride are not shifted.[2]

TABLE III

Intensities Ratio for Antistokes and Stokes Frequencies of PCl_3

ω	$i_{\tilde{A}}/i_{\tilde{S}}$ observed	$i_{\tilde{A}}/i_{\tilde{S}}$ calculated
189	0,37	0,38
259	0,30	0,27
511	0,08	0,077

5. We could not obtain the Raman spectra of bismuth chloride in alcohols and in acetone, on account of the quick photolysis that takes place. Very diffuse lines were obtained with BCl_3 in hydrochloric acid solutions. The frequencies 110, 236 and 279 cm.$^{-1}$ are in good agreement with the data of Bhagavantam[9] and of Daure.[6]

Our results show the impossibility of explaining the shifts solely by the difference in dipole moments of the mixture components. If their absence in mixtures of $AsCl_3$ and C_6H_6 and of $AsCl_3$ and CCl_4 can be ascribed to the non-polarity of the solvents, then it is difficult to explain from this point of view, for example, the shifting of the halide frequencies and the non-shifting of the alcohol frequencies in mixtures of $AsCl_3$ ($\mu = 2 \cdot 1 \times 10^{-18}$) or $SbCl_3$ ($\mu = 3-4 \times 10^{-18}$) with alcohols ($\mu = 1 \cdot 65-1 \cdot 70 \times 10^{-18}$).

We have suggested that the dipoles of the second compound can shift the frequencies of the first only when the force constant of the bond, active in Raman spectra of the first compound is weak enough[1, 14]. It must be noted in this connection that usually the force of the bond changes in the same direction as the bond energy and its anharmonicity.‡ Our suggestion is further confirmed by the data of some other authors.[14]

It is essential to note that in all the investigated solutions of $AsCl_3$ and of $SbCl_3$ the ratio ω_{iv}/ω_{iii} is constant and remains the same as in the pure substance. This can be ascribed to the smallness of the effect of the influence of the solvent on the geometric configuration of the molecules of the solute. Of course, this conclusion cannot be generalised.

It is to be further mentioned, that one of us (Kortchagin[5]) has measured the frequency 1048 cm.$^{-1}$ of the NO_3^- ion in solutions of potassium and

‡ See the comparison of the force constants for PCl_3, $SbCl_3$ and $AsCl_3$ by Kohlrausch[10] and Andrews and Murray.[11]

sodium nitrates, in presence of Li^+ ions and of sucrose in very high concentrations. No shifts were discovered. This is to be ascribed to the screening-effect of the solvent-envelopes.[12] It is in good agreement with Grassmann's[13] data, wherein there is found only a small displacement of this frequency by $LiNO_3$, in comparison with HNO_3 and no shifts on dilution of the HNO_3 solutions.§

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§ The precision of the measurements was 2-3 $cm.^{-1}$, on account of the breadth of the lines in these solutions.

ADIABATIC AND ISOTHERMAL COMPRESSIBILITIES OF LIQUIDS

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1. *Introduction*

Tyrer[1] was the first investigator who recognised that the compressibility values obtained by the early workers were neither truly adiabatic nor truly isothermal. He determined the adiabatic compressibilities for a few liquids with a piezometer having a volume of 500 c.c. The changes in volume were observed by allowing the liquid to expand in a calibrated capillary tube. With the aid of the usual thermodynamic relation, he calculated the isothermal compressibility in each case. In his first paper he took the values of variation of specific volume with temperature $\left(\frac{\partial v}{\partial T}\right)_p$ and specific heat at constant pressure C_p from different authors. In his second paper he determined $\left(\frac{\partial v}{\partial T}\right)_p$ and took C_p from other authors. He had to redetermine $\left(\frac{\partial v}{\partial T}\right)_p$ since some of the previous values were wrong and affected the isothermal compressibility to a considerable extent. Following the method of Tyrer and using the same type of piezometer Dakshinamurti[2] studied the compressibility of some essential and vegetable oils with a view to connect it with the phenomenon of light scattering. Recently Bhagavantam and Rao[3] studied the compressibility of ordinary and heavy water in relation to their light scattering and allied physical properties.

Subsequent to the work of Tyrer, the subject of light scattering in liquids has been greatly developed and we have to-day a large volume of experimental data in respect of this branch of physics. The Einstein-Smoluchouski theory of density scattering connects the isothermal compressibility of liquids with the intensity and depolarisation of the scattered light and thus an experimental determination of the adiabatic compressibility and the calculation therefrom of the isothermal compressibility assumes fresh importance. Krishnan[4] and subsequently some others have obtained the intensity of the scattered light in several liquids and sought to verify the

Einstein-Smoluchouski theory but had to depend upon doubtful values of compressibility drawn from the older literature except in such cases as have been studied by Tyrer. The latter author has studied only about a dozen liquids whereas a few hundreds of liquids have been studied in respect of light scattering. It is also felt that the procedure adopted by Tyrer in borrowing the physical constants required for the calculation of the isothermal compressibility from other investigators is less satisfactory than obtaining all of them from one author. Accordingly the present investigation is undertaken and both the adiabatic and isothermal compressibilities of a few liquids are given by determining the other physical constants also for the same sample of the liquid. The Einstein-Smoluchouski formula for the intensity of light scattering is then verified. The specific volume and the variation of specific volume with temperature have been determined by a special type of pyknometer. The specific heat at constant pressure is determined by an electrical method.

2. *Experimental Methods*

Apparatus I.—The piezometer used in the present investigation is of the type used by Tyrer and by Dakshinamurti. Slight modifications are introduced to suit the present work. It consists of the cylindrical container A (Fig. 1) to which is joined the bulb B and the capillary tube T. The bulb B

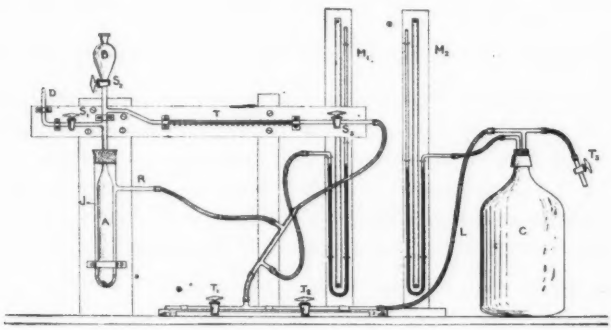

FIG. 1
Piezometer

is completely filled with the liquid and the piezometer is evacuated by the side tube D. The liquid is then admitted into the container A by turning the stop-cock S_2. Care is taken to see that no air bubbles stick inside the piezometer and that the liquid fills up the whole of the capillary tube. A drop of clean mercury is admitted through the stop-cock S_3 and is drawn

in the form of a pellet into the capillary tube by suitably inclining the piezometer, opening the stop-cock S_2 and blowing air through S_3. The side tube R of the outer jacket J is connected to S_3, and this is connected to the pressure system. In the previous methods of Tyrer and of Dakshinamurti, the liquid is compressed by the help of a pump, the pressure is noted and then suddenly released. The shift of the mercury pellet in the capillary resulting from the adiabatic expansion of the liquid is noted. As the compression is caused with the help of a pump, it cannot be considered as truly adiabatic and hence readings are taken only when the pressure is released. In the present investigation, an improvement has been made in the method of application of pressure as will be seen from Fig. 1. The arrangement enables both an application and a release of pressure to be effected adiabatically. The pressure arrangement consists of a carboy C into which air is pumped through the stop-cock T_3. The carboy C is the reservoir and the pressure in the reservoir is indicated by the manometer M_2. The leading tube L connects the reservoir to the stop-cock T_2. When T_1 is open and T_2 is closed, the liquid in the piezometer is at atmospheric pressure. When T_1 is closed and T_2 is open, the liquid is compressed and the manometer M_1 shows the pressure to which the liquid has been submitted. The shift of the mercury pellet caused by this compression gives the resulting change in volume. Then T_2 is closed when the liquid still remains compressed at the previous pressure and T_1 is suddenly opened to the outer air. The pressure in M_1 falls to that of the atmosphere and the shift of the mercury pellet caused by a release of this gives the resulting change in volume. The mean of the two results may be taken for purposes of calculating the adiabatic compressibility. A carboy having a large volume is selected so that the manometer M_2 may not fall off rapidly. The method described above has the advantage that when once the carboy having a large volume is filled up with air at a high pressure, a set of readings may conveniently be taken by successively opening and closing the proper stop-cocks. The arrangement also enables us to measure the changes in volume caused both by the adiabatic expansion and compression of the liquid.

Capillary tubes have been avoided in constructing the manometers M_1 and M_2 since they introduce errors due to capillarity. It may be mentioned here that stop-cocks sometimes give trouble and slight leaks introduce appreciable errors. For many of the organic liquids studied, a warm mixture of dextrose and glycerol serves the purpose of a good stop-cock grease.

Apparatus II.—Since the type of piezometer which was used by Tyrer and a modification of which is described in the present investigation is elaborate and inconvenient to handle, a compact type of piezometer has

also been designed by the author. In this type (Fig. 2) the body A of the piezometer which is horizontal is surrounded by the jacket J. L_1 is the side

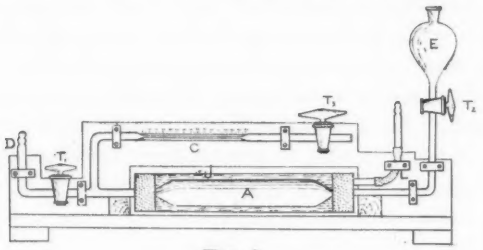

FIG. 2
Piezometer

tube through which pressure is applied. The piezometer is first evacuated and the liquid which is kept in the bulb E is allowed to flow into the piezometer as before. C is the capillary joined to the stop-cock T_3. T_3 and L_1 are joined and attached to the pressure apparatus, which is the same as that used with the piezometer of Type 1. The new type of piezometer is compact and fixed on a horizontal board which can be conveniently handled. Besides compactness, this apparatus possesses the additional advantage that the dead space is made smaller than that in the previous type of piezometer. The volume of the container in this case is also comparatively large and a capillary tube of a wider bore could be used, thus eliminating the capillary effects.

Constants of the Apparatus.—The volume of the piezometer has been found by filling it with distilled water. The capillary used with apparatus I is part of a broken mercury thermometer having a range 0–360° C. The mean area of cross-section of the capillary is 0·0003385 sq. cm. and each division on the thermometer corresponds to 0·5673 mm. The volume of the piezometer is found to be 73·5 c.c. at 28° C. The capacity of piezometer II is found to be 135·5 c.c. at 31° C. and the capillary has a mean area of cross-section of 0·0006463 sq. cm. The scale used behind the capillary is an ordinary millimetre scale.

Effect due to the Change in the Volume of the Container.—It may easily be shown that if $\beta_{\phi l}$ is the adiabatic compressibility of the liquid and $\beta_{\phi c}$ is that of the material of the container

$$\beta_{\phi l} \text{ (real)} = \beta_{\phi l} \text{ (apparent)} + \beta_{\phi c}$$

both in the case of expansion and of compression.* The compressibility of

* The equivalent relation used by Tyrer is $\beta_{\phi l}$ (real) $= \beta_{\phi l}$ (apparent) $+ \beta_{\phi c}/P$. This is apparently incorrect but the error introduced is not very serious.

soda glass is taken as $2 \cdot 2 \times 10^{-6}$ in accordance with the investigations of Amagat.[5]

Dead Space of the Piezometer.—That part of the piezometer where pressure cannot be applied both internally and externally may be termed the dead space. In the piezometer used in the present investigation, the dead space is made as small as possible by taking tubes of small area of cross-section in connecting the main body of the piezometer to the stop-cocks, etc. The shift is always increased due to the dead space and the compressibility is apparently enhanced. If the shape of the dead space is cylindrical, the actual increase in volume due to the dead space can be evaluated. Only a rough estimate may, however, be made in the piezometer used. Knowing the dimensions of the tube covering the dead space and assuming $1/K = 2 \cdot 2 \times 10^{-6}$ and $n = 2 \cdot 93 \times 10^{11}$, the change in volume due to dead space comes out as 0·0003689 c.c. for a pressure of 50 cm. of mercury. This corresponds to a mercury pellet shift of nearly one division on the scale. The shifts observed are usually of the order of about 80 divisions. It may therefore be concluded that the dead space in the present apparatus does not introduce large errors at moderate pressures.

Effect of Filling the Outer Jacket with Water.—If the outer jacket surrounding the body of the piezometer is left empty, it has been found that the readings taken by the application and release of pressure differed from each other considerably. This is traced and attributed to the fact that when air is compressed into the jacket, it is heated and begins to heat the liquid in the piezometer. The outer jacket has accordingly been completely filled with water and the values obtained both for expansion and compression are then found to agree with each other. There is yet another advantage of filling the jacket with water. The volume into which the air from the reservoir is compressed is made small and hence the manometers M_1 and M_2 show almost the same readings and the reservoir manometer M_1 will not fall off rapidly when successive readings are taken.

Capillary Forces and the Shifts.—In order that we may get a measurable shift of the mercury pellet, it is necessary to take a large volume of the liquid and a fine capillary. If the capillary is however very fine, it introduces an error as the pellet moves rather slowly due to the capillary effects thus rendering the expansion or compression non-adiabatic. Apparatus I has a finer capillary and the values obtained with it are slightly higher than those observed with apparatus II. The capillary attached to apparatus II has a wider bore. Too narrow a capillary has the advantage of giving a large shift but is not desirable from the above point of view.

TABLE I

Adiabatic Compressibilities

Liquid	Temp. °C.	$\beta\phi \times 10^6$ Author	$\beta\phi \times 10^6$ Tyrer	$\beta\phi \times 10^6$ (about 23° C.) Parthasarathy
Carbon disulphide ..	28·0	66·47	63·72	60·2
Chloroform	30·4	76·11	74·36	67·1
Chlorobenzene	32·4	57·78	60·66	53·6
Benzene	28·2	71·70	70·98	66·8
Methyl alcohol	27·6	103·3	107·4	98·9
Carbon tetrachloride ..	28·0	77·76	77·74	72·6
Water	30·8	43·10	44·45	44·9
Hexane	27·5	123·8	..	122·7
Heptane	27·6	105·0	..	108·1
n-Propyl alcohol ..	28·0	90·82	..	81·9
Iso-Propyl alcohol ..	30·0	92·60	..	84·1
Butyl alcohol	29·4	76·26	..	71·5
Amyl alcohol	29·2	78·39	..	..
Acetone	29·2	91·38	..	87·4
Acetic anhydride ..	30·0	67·40	..	48·6
Anisol	31·6	52·20	..	45·7
Acetophenone	30·0	49·33	..	41·3
Cyclohexane	31·0	84·88	..	81·9
Cyclohexanone	30·8	59·80	..	50·8
Cyclohexanol	31·9	55·50	..	40·2
Paraldehyde	33·4	86·84	..	..
Formaldehyde .. .. (aqueous solution)	31·6	45·50	..	..
Benzyl acetate	32·8	50·31	..	..
Amyl acetate	30·1	92·27	..	..

Effect of Viscosity.—When the capillary is very fine, viscous liquids also give slow shifts and similar reasoning as above will show that the values are not perfectly adiabatic. In the present investigation the more viscous liquids have been studied with piezometer II which has been specially made to give large shifts even with a wide capillary tube.

3. *Adiabatic Compressibility of Liquids*

Liquids supplied by either Merck or Schering Kahlbaum are used. They are carefully distilled and the middle fraction is collected. The specific gravity is taken as a test for the purity of the liquid. In Table I are given the adiabatic compressibilities obtained in the present investigation. Apparatus I has been employed in most cases but in a few liquids which are particularly viscous, apparatus II has been used. Tyrer's values are available for seven of the liquids studied here and these are given for comparison, after reduction to the appropriate temperatures. Parthasarathy[6] has recently obtained the adiabatic compressibilities by the method of diffraction of light by ultra-sonic waves and his values are contained in the last column.

The considerable discrepancy between the author's and Parthasarathy's values in the cases of acetic anhydride and cyclohexanol may be noted. For all the other liquids, the agreement between the two sets of values, taking into account the difference of temperatures, is fairly satisfactory.

4. *Specific Volume and its Variation with Temperature*

The densities of the liquids at different temperatures are found with a special type of pyknometer already described by Dakshinamurti.[2] The volume of the pyknometer used in the present investigation is 11·2214 c.c. at 27·3° C. Allowance is made for the expansion of the glass of the pyknometer by taking its coefficient of cubical expansion as 9×10^{-6}.

The densities and therefrom the specific volumes of the liquids at about six different temperatures are determined in each case. The specific volume at any temperatures can be represented by the equation

$$v_t = v_0 + \alpha\,(t - 30) + \beta\,(t^2 - 30^2)$$

where v_0, α and β are constants. These constants are determined by taking three different values of v_t at three temperatures. From this equation $\left(\frac{\delta v}{\delta T}\right)$ at any temperature can be calculated. The constants obtained in respect of the various liquids studied are given in Table II.

TABLE II

Dependence of Specific Volume on Temperature : Constants

Liquid	Range °C.	v_0	α	β
Hexane	25–55	1·53741	$0 \cdot 0_3389$	$0 \cdot 0_4282$
Heptane	25–65	1·48223	$0 \cdot 0_3866$	$0 \cdot 0_4155$
Methyl alcohol	25–60	1·27893	$0 \cdot 0_2327$	$-0 \cdot 0_4271$
n-Propyl alcohol	25–65	1·25943	$0 \cdot 0_2233$	$-0 \cdot 0_4176$
Iso-Propyl alcohol ..	25–65	1·28689	$0 \cdot 0_2105$	$0 \cdot 0_5916$
Butyl alcohol	30–60	1·24450	$0 \cdot 0_3836$	$0 \cdot 0_5417$
Amyl alcohol	30–65	1·24515	$0 \cdot 0_3789$	$0 \cdot 0_5465$
Acetone	30–50	1·28468	$0 \cdot 0_2119$	$0 \cdot 0_5410$
Acetic anhydride	30–70	0·93716	$0 \cdot 0_3967$	$0 \cdot 0_5125$
Carbon disulphide ..	25–45	0·80142	$0 \cdot 0_3350$	$0 \cdot 0_5911$
Chloroform	30–50	0·68055	$0 \cdot 0_2125$	$-0 \cdot 0_5556$
Chlorobenzene	30–65	0·91280	$0 \cdot 0_3736$	$0 \cdot 0_5191$
Benzene	25–55	1·15211	$0 \cdot 0_3566$	$0 \cdot 0_4119$
Anisol	30–65	1·01645	$0 \cdot 0_3387$	$0 \cdot 0_5710$
Carbon tetrachloride ..	25–50	0·63516	$0 \cdot 0_3865$	$-0 \cdot 0_6971$
Acetophenone	30–65	0·99902	$0 \cdot 0_3726$	$0 \cdot 0_5267$
Cyclohexane	30–70	1·30077	$0 \cdot 0_3882$	$0 \cdot 0_5857$
Cyclohexanone	30–70	1·06779	$0 \cdot 0_2109$	$-0 \cdot 0_6263$
Cyclohexanol	30–70	1·07255	$0 \cdot 0_3858$	$0 \cdot 0_6277$
Paraldehyde	30–70	1·01920	$0 \cdot 0_3623$	$0 \cdot 0_5632$
Formaldehyde (solution) ..	30–70	0·95245	$0 \cdot 0_3503$	$0 \cdot 0_5129$
Benzyl acetate	30–70	0·95713	$0 \cdot 0_3604$	$0 \cdot 0_5319$
Amyl acetate	20–60	1·16369	$0 \cdot 0_2255$	$-0 \cdot 0_4418$
Water	25–60	1·00439	$0 \cdot 0_3387$	$-0 \cdot 0_6350$

TABLE III

Adiabatic and Isothermal Compressibilities

Liquid	Temp. °C.	$\beta_\phi \times 10^6$	v	$\left(\frac{\delta v}{\delta_\tau}\right)_p \times 10^6$	C_p	$\beta_\tau \times 10^6$	γ
Hexane	27·5	123·8	1·532	1940	0·516	158·5	1·28
Heptane	27·6	105·0	1·478	1622	0·503	130·8	1·25
Methyl alcohol ..	27·6	103·3	1·275	1774	0·647	131·1	1·27
n-Propyl alcohol ..	28·0	90·82	1·257	1344	0·655	106·8	1·18
Iso-Propyl alcohol..	30·0	92·60	1·287	1600	0·686	113·9	1·23
Butyl alcohol ..	29·4	76·26	1·244	1081	0·695	86·16	1·13
Amyl alcohol ..	29·2	78·39	1·244	1061	0·547	90·51	1·15
Acetone	29·2	91·38	1·282	1429	0·529	113·4	1·24
Acetic anhydride ..	30·0	67·40	0·937	1042	0·394	88·96	1·32
Carbon disulphide..	28·0	66·47	0·799	860	0·239	94·72	1·43
Chloroform ..	30·4	76·11	0·681	912	0·280	108·2	1·42
Chlorobenzene ..	32·4	57·78	0·915	860	0·334	75·69	1·31
Benzene ..	28·2	71·70	1·149	1237	0·416	95·06	1·33
Anisol	31·6	52·20	1·018	836	0·461	63·18	1·21
Carbon tetrachloride	28·0	77·76	0·633	811	0·207	114·4	1·47
Acetophenone ..	30·0	49·33	0·999	886	0·453	62·05	1·26
Cyclohexane ..	31·0	84·88	1·302	1413	0·285	124·5	1·47
Cyclohexanone ..	30·8	59·80	1·068	1074	0·488	76·13	1·27
Cyclohexanol ..	31·9	55·50	1·074	876	0·483	66·42	1·20
Paraldehyde ..	33·4	86·84	1·023	1045	0·459	104·1	1·20
Formaldehyde (solution) ..	31·6	45·50	0·953	585	0·815	48·75	1·07
Benzyl acetate ..	32·8	50·31	0·958	215	0·245	51·77	1·03
Amyl acetate ..	30·1	92·27	1·164	33	0·507	92·28	1·00
Water	30·8	43·10	1·004	365	1·004	44·07	1·02

5. *Specific Heat at Constant Pressure*

The data for specific heat at the room temperature are not available for all the liquids studied in the present paper. It is also thought desirable to determine the specific heat for the same sample of the liquid for reasons already stated. An electrical method is employed for this purpose and the values obtained for the liquids are included in Table III.

6. *Isothermal Compressibility*

The constants that have been measured in the foregoing sections permit us to calculate the isothermal compressibility from the well-known thermodynamical equation

$$\beta_T = \beta_\phi + \frac{T\left(\frac{\partial v}{\partial T}\right)_P^2 \times 1{\cdot}013 \times 10^6}{J\, v\, c_P}$$

in which the various letters have the usual significance. The values of β_T so calculated and the ratio of β_T to β_ϕ which is equal to the ratio of specific heats are noted down for each liquid in Table III.

7. *Comparison of Calculated and Observed Intensities of Light Scattering*

The ratio of intensities I_1 and I_2 of the light scattered by two liquids is given by the relation

$$\frac{I_1}{I_2} = \frac{\beta_{T1}\,(n_1^2 - 1)^2\,(6 + 6\,\rho_1)\,(6 - 7\,\rho_2)}{\beta_{T_2}\,(n_2^2 - 1)^2\,(6 + 6\,\rho_2)\,(6 - 7\,\rho_1)}$$

where β_T, n and ρ stand respectively for the isothermal compressibility, the refractive index and the depolarisation of scattered light. The values calculated with the help of the above equation and the constants given in the foregoing tables are compared with the observed values in Table IV. All the liquids are compared with benzene, the intensity of the light scattered by which is taken as 3·2.† The refractive index is measured with an Abbe refractometer for several of the liquids. In others, it is taken from the data of other observers. ρ and I are taken from the existing literature. The agreement between the calculated and observed values is satisfactory in a number of cases.

† This corresponds to Ether = 1.

TABLE IV

Comparison of Calculated and Observed Intensities of Light Scattering

Liquid	$\beta_T \times 10^6$	n	$\rho \times 100$	I (Observed)	I (Calculated)
Hexane	158·5	1·372	9·95	1·0	1·18
Heptane	130·8	1·391	10·0	1·0	1·10
Methyl alcohol ..	131·1	1·334	4·9	0·46	0·68
n-Propyl alcohol ..	106·8	1·390	5·8	0·57	0·81
Iso-Propyl alcohol ..	113·9	1·382	3·9	0·53	0·79
Butyl alcohol ..	86·16	1·390	7·5	0·60	0·68
Amyl alcohol ..	90·51	1·397	8·0	0·74	0·75
Acetone	113·4	1·369	25·0	0·81	1·18
Acetic anhydride ..	88·96	1·395	43·0	1·01	1·76
Carbon disulphide ..	94·72	1·656	62·0	13·0	12·9
Chloroform	108·2	1·453	24·2	1·26	1·78
Benzene	95·06	1·495	43·0	3·15	3·20
Chlorobenzene ..	75·69	1·514	60·0	4·63	5·18
Anisol	63·18	1·508	50·0	3·52	2·84
Carbon tetrachloride ..	114·4	1·468	6·0	1·02	1·34
Acetophenone ..	62·05	1·510	70·0	5·66	7·25
Water	44·07	1·333	6·2	0·2	0·23

Summary

A glass piezometer similar to that used earlier by Tyrer has been constructed. The adiabatic compressibility, variation of specific volume with temperature and the specific heat at constant pressure have been measured for 24 liquids after careful purification. The isothermal compressibility and the ratio of specific heats are obtained in each case by calculation.

A comparison is made of the calculated figures with the observed values in respect of the relative intensities of light scattering in these liquids and good argeement is obtained.

In conclusion the author desires to express his grateful thanks to Prof. S. Bhagavantam under whose guidance the above work has been done.

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CHEMICAL COMPOSITION OF *VITIS QUADRANGULARIS* (WALL)

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Vitis quadrangularis is a tender climber with fleshy quadrangular stems and is distributed all over the hotter parts of India. In Sanskrit it is known as *Asthisamhara*, in Hindi as *Nallar* and Telugu as *Nallеru*. When cut and rubbed on the skin the stem produces a prickly sensation which lasts a considerable time.

The plant (stems, leaves) is commonly used as a green vegetable. The juice is added to pastry with a view to improve their texture and make them swell when fried. The ash is frequently employed in the place of baking powder. The fresh or dried stems, leaves and tender shoots hold a prominent place as household remedies mainly in connection with affections of the digestive system. In certain parts of India the tender shoots of the plant are ashed in closed vessels and administered in dyspepsia and indigestion. The drug seems also to find use in cases of asthma, scurvy and other ailments.[1] No chemical investigation appears to have been done on this drug till now.

The following results give a general idea of the composition of the air-dried drug :

	%
Moisture	13·1
Ash	18·2
Proteins	12·8
Carbohydrates	36·6
Fibre	15·6
Fat and Wax	1·0
Mucilages and Pectins	1·2

A preliminary test for alkaloids using Prollius's fluid showed that there was none. The following solvents were used in succession for extraction on a small scale and the extracts were examined :

		%	
1.	Petrol (60°–80°)	.. 2·7	Wax and some chlorophyll.
2.	Ethyl ether ..	.. 0·4	Chlorophyll and some resin.
3.	Carbon tetrachloride	.. 0·2	Chlorophyll and some wax.
4.	Alcohol	.. 2·1	Sugars and inorganic salts.
5.	Water	.. 5·4	Gums, pectins and sugars.

Since the most considerable portions were extracted by petrol, alcohol and water several kilograms of the drug were extracted with these three solvents in succession and the extracts were studied in detail. The wax present in the petrol extract was isolated in the form of a yellow solid melting at about 80° and its general properties have been recorded. About 50 per cent. of the alcohol extract consisted of mineral matter comprising mostly of sodium and potassium salts (carbonates and chlorides). The remaining resinous portion contained some tartaric acid and a small quantity of yellow flavone pigments. The former was characterised as the acid potassium tartrate; the latter was too small to be isolated and studied. The final aqueous extract was found to undergo fermentation readily to give alcohol. Besides sugars it contained gums and pectins which could be thrown out by the addition of alcohol. Calcium was found to be present in the ash obtained from the precipitated solid.

An analysis of the sap of the green plant gave results somewhat similar to that of the aqueous extract. A microscopic examination of a section of the stem indicated the existence of plenty of small crystals of calcium oxalate. The irritating action of the freshly cut stem surface may be due to the penetration of these tiny crystals into the skin. The presence of this salt could be further established by extracting the air-dried material with dilute hydrochloric acid and neutralising the extract with ammonia.

The ash which formed 18·2 per cent. of the air-dried material was analysed in detail qualitatively and quantitatively. It was found to consist mostly of the carbonates and to a smaller extent of the phosphates of sodium, potassium, magnesium and calcium. The total absence of chlorides in the ash was remarkable since they were found to be present in the mineral matter that was isolated from the alcoholic extract. This is obviously due to the loss of the chlorides by volatilisation during the course of ashing. Such loss has been noted by other workers.[2]

From the above results there seems to be no organic compound in *Vitis quadrangularis* that could account for its medicinal properties. The high percentage of the ash in the plant and its composition may explain the beneficial effect in cases of dyspepsia and indigestion. Since the plant has been employed as a remedy against scurvy and is consumed to a large extent as a vegetable and since the sap and water extract have very high reducing power, experiments were made to estimate the amount of carotene and ascorbic acid (Vitamin C) present in the material. The value for carotene was 267*r* per 100 grams and hence in this respect this vegetable occupies a middle place. On the other hand the content of Vitamin C was remarkably high being about 400 mg. per 100 grams of the fresh material. The value

obtained for the freshly expressed sap was still higher and hence *Vitis quadrangularis* is one of the vegetable sources which top the list regarding this vitamin as shown in the following table :—

Vegetable Source	Vitamin C content in mg. per 100 grams of the material	Literature reference
Vitis quadrangularis (Shoots and leaves) ..	398	This paper
Do. Sap ..	479	Do.
Rose hips	308–416	Goldberg and Walsh[3]
Indian Gooseberry	413	Damodaran and Srinivasan[4]
Drumstick	216	
Cashew apple	203	
Guava	299	Ranganadhan[5]
Parsley	280	
Amaranth leaves	174·9	
Green chillies	143·0	
Cabbage	132·1	
Orange juice	102·0	
Cauliflower	65·8	
Spinach	36·9–63·7	

Experimental

The fresh plant was collected from the surroundings of Waltair, and after cleaning and drying in the sun ground into powder in a coffee mill. There was about 90 per cent. loss of weight on drying. The preliminary analysis for the proximate components was done by standard methods adopted by the A.O. A.C. ; the results are given in the introductory part.

100 g. of the powdered drug were extracted with Prollius's fluid for 24 hours in the cold and the extract examined for the presence of alkaloids. The test was negative. The same weight of the drug was extracted in a

soxhlet apparatus successively with various solvents. The summary of the results of this extraction has been given in the introductory part.

The Petroleum extract: *Wax.*—For purposes of a detailed study of the important fractions several kilograms of the dry powder were extracted first with light petroleum (b.p. 60°–80°) in a continuous extractor for 12 hours. After recovering the solvent from the extract, a greenish yellow viscid mass was obtained. When treated with ether or hot benzene most of the green colouring matter could be removed and a yellow wax was left behind. The most convenient method of obtaining the wax pure was to boil the viscous solid with alcohol for 15 minutes, filter hot and allow the solution to cool. The yellowish solid that was deposited looked clean; it was subsequently filtered and washed with small quantities of alcohol. The process was once again repeated for further purification (yield 1 per cent.). The product had all the properties of a wax. It was greasy to the touch and left a grease spot when rubbed on paper. It was insoluble in water and cold dilute alcohol and floated on water. But it dissolved easily in benzene, carbon tetrachloride, chloroform and ether. Its properties were examined by the standard methods and they are recorded below:—

Colour	Light yellow
Melting point	78°—80°
Acid value	27·5
Saponification value ..	121·8
Iodine value	11·2
Unsaponifiable matter ..	49·6

The brown amorphous unsaponifiable matter gave rise to a faint yellow product melting at 83°–86° when crystallised from alcohol. It contained some sterols also since it gave a violet colour when to a chloroform solution acetic anhydride and sulphuric acid were added.

Alcohol extract: *Mineral matter.*—The residue left after the extraction with petrol was subsequently extracted in the same apparatus with methylated spirit for 12 hours. When the extract was concentrated to a small bulk it deposited a colourless crystalline solid which could be separated pure by filtering and washing with small quantities of alcohol. It was inorganic in nature and consisted of the carbonates and chlorides of potassium and sodium. It amounted to nearly 50 per cent. of the alcoholic extract or one per cent. of the air-dried drug. The remainder of this fraction obtained on completely evaporating the solvent was a resinous mass which could not be made to crystallise. After extracting it with hot water, the water-insoluble resin was found to possess neither taste nor smell. It dissolved in alkali and was partly soluble in sulphuric acid to give a green solution. The aqueous

extract was acidic to litmus, gave strong tests for sugars (glucose as osazone) and gave indications for the presence of flavone pigments.

The hot water extract obtained above was treated with neutral lead acetate solution and the precipitated lead salt was isolated and decomposed in aqueous suspension with hydrogen sulphide. After filtering off the sulphide of lead the aqueous solution was concentrated to a small bulk. A small quantity of an amorphous gummy solid was thus obtained and though this gave tests for flavones no crystalline solid could be isolated and the quantity was too little to enable further investigation to be carried out.

After removing the neutral lead acetate precipitate the aqueous mother liquor was treated with excess of basic lead acetate and the yellow precipitate thereby obtained was decomposed with hydrogen sulphide as before. When the final aqueous solution was concentrated *in vacuo* and treated with an aqueous solution of potassium acetate and subsequently with alcohol a colourless solid was obtained. This was identified as potassium hydrogen tartrate from its properties and reactions.

The final mother liquor was deleaded by passing hydrogen sulphide and concentrated *in vacuo*. No crystalline substance could be isolated, but the amorphous residue was saccharine in nature and gave rise to a good yield of glucosazone on being treated with phenylhydrazine hydrochloride, sodium acetate and acetic acid.

Hence the alcoholic extract was found to contain a good amount of mineral salts, some alkali soluble resin, sugars, some tartaric acid and a trace of flavone pigments.

Water extract : *gums and pectins*.—The plant material left after extraction with alcohol was subsequently boiled up with water and filtered hot. A brownish, highly viscous extract was thereby obtained and this was found to ferment rapidly on keeping to give rise to alcohol. When twice the volume of alcohol was added to it a white gummy solid separated out. This amorphous substance underwent hydrolysis easily to give products which reduced Fehlings solution and on incineration left an ash containing calcium, showing thereby that pectins were present. The solution left after the removal of the gums and pectins gave good tests for glucose (osazone) and on concentration and incineration yielded inorganic matter.

Examination of the ash.—The ashing was effected in large platinum basins. A qualitative analysis revealed the following as major components : calcium, magnesium, potassium and sodium, carbonates, phosphates and silica. Iron, aluminium and sulphate were found in traces. For the quantitative estimation the residue insoluble in dilute hydrochloric acid was taken

as silica. Phosphoric acid was estimated by the volumetric method through phosphomolybdate. The carbonate was determined gravimetrically by decomposing the ash with excess of acid and absorbing the carbon dioxide evolved with soda lime. Lime was estimated volumetrically as the oxalate and magnesia by precipitation with 8-hydroxyquinoline in ammoniacal solution. Potassium and sodium were weighed as chlorides and after estimating the former as the perchlorate the latter was obtained by difference. The following table gives the average of several analyses :—

	%
SiO_2	3·00
P_2O_5	4·13
CO_2	23·95
CaO	18·44
MgO	15·79
K_2O	17·54
Na_2O	13·16

Isolation of calcium oxalate.—200 g. of the powdered drug were extracted with petrol and then with alcohol and the residue boiled with 1 per cent. hydrochloric acid for 2 hours. The acid extract was concentrated to a small bulk on a water-bath and twice its volume of alcohol added so as to precipitate gums and pectins. After filtration, the filtrate was rendered slightly alkaline with ammonia and then acidified with acetic acid. On heating the solution for half an hour on a water-bath a copious white precipitate settled down. It responded to all tests for calcium and oxalic acid and was identified as calcium oxalate.

Estimation of Carotene

About 10 grams of the fresh material were boiled for an hour with 20 per cent. alcoholic potash. After filtration the residue was soaked with aqueous ether and extracted with acetone repeatedly till the extract was colourless. The combined extracts were concentrated and the residue taken up in petroleum ether. Xanthophyll was removed by shaking the above solution with small quantities of 85 to 90 per cent. methyl alcohol. The petroleum solution of carotene was then made up to a known volume and compared with a 0·2 per cent. solution of potassium dichromate in a comparator. The amount of carotene was obtained from a standard curve.[6] The average value from several determinations was 267 *r* of carotene for 100 grams of the plant material.

Vitamin C.[7]—10 Grams of the freshly cut material were ground up with 20 per cent. trichloroacetic acid (6·5 c.c.) and specially purified sand and filtered through muslin. The extraction was repeated 3 times with fresh

portions of the acid solution. The combined extract was made up to 100 c.c. with water and filtered through a filter paper. The concentration of trichloroacetic acid in this solution was thus kept at about 5 per cent. This solution was titrated against 1 to 5 c.c. of standardised 2 : 6 dichlorophenolindophenol solution within 1 to 2 minutes. The dye solution was prepared by dissolving 0·05 g. in 100 c.c. of water and standardised against a solution of ascorbic acid whose purity had been tested with a standard solution of iodine. The average of several determinations using the tender portions of the stem and using 1 to 5 c.c. of the dye solution was 398 mg. per 100 grams of the plant. The fibrous bottom portions of the stem gave a lower value, 232 mg. The freshly expressed sap was diluted with water and sufficient trichloroacetic acid so as to make its concentration 5 per cent. and then titrated against the dye solution. In another set of experiments trichloroacetic acid was omitted. In both cases, however, the same values for ascorbic acid were obtained : 479 mg. per 100 grams. The quality of the sap deteriorated rapidly on keeping. After about 24 hours the loss was found to be about 25 per cent.

Summary

A detailed chemical examination of the stems and leaves of *Vitis quadrangularis* for the organic components and mineral matter has been made. Besides gums and pectins, a yellow wax and tartaric acid as the acid potassium salt were isolated. The presence of calcium oxalate crystals may account for the irritating action of the freshly cut stem on the skin. The plant contains a high percentage of mineral matter and the ash consists mostly of the carbonates of magnesium, calcium and the alkali metals. As a source of carotene it occupies a middle place and it contains a remarkably high percentage of ascorbic acid (Vitamin C).

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ON THE INVERSES OF A CIRCLE WITH RESPECT TO A TETRAD OF FIXED CIRCLES AND THEIR ORTHOGONAL TETRAD*

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(Communicated by Professor A. Narasinga Rao)

1. Let C_i $(i = 1, 2, 3, 4)$ be four circles and S_i the four circles respectively orthogonal to sets of three chosen from C_i. The main object of this paper is then to establish the following results.

If the inverses of a point P w.r.t. the circles C_i lie on a circle, then the inverses of P w.r.t. S_i also lie on a circle. The locus of such points P is an octavic curve Γ_1 having quadruple points at the circular points at infinity (1·1)

The totality of circles Σ whose inverses w.r.t. C_i have a common orthogonal circle as also the inverses w.r.t. S_i consists of the four coaxal systems respectively conjugate to the four systems defined by the pairs C_i, S_i ; $(i = 1, 2, 3, 4)$ and a family of circles whose centres lie on a quartic curve. (1·2)

If the inverses of a circle Σ. w.r.t. the circle C_i have a common orthogonal circle Σ', the transformation in circle-space carrying Σ to Σ is the involutoric cubic transformation whose singular points are those representing the circles S_i and whose fixed points represent the circles cutting the circles C_i at equal angles. (1·3)

Lastly the following theorem relating to the Miquel-Clifford configuration is proved.

If the inverses of a point P w.r.t. n concurrent circles C_i lie on a circle then the inverses of P w.r.t. every concurrent set of n circles of the Miquel-Clifford configuration generated by the circles C_i also lie on a circle. (1·4)

2. It is well known that the ∞^3 circles of a plane π may be represented by the points of a projective space S_3, the ∞^2 point circles corresponding to points on a quadric Ω called the Absolute. Let us represent, for convenience, by the same symbol both the circle on π and its corresponding point in S_3. Let Δ_1, Δ_2 be the two tetrahedra whose vertices represent C_i and S_i so

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that Δ_1, Δ_2 are reciprocals of each other in regard to Ω. If the inverses of a point P on π w.r.t. the circles C_i are concyclic, it is easy to see that in S_3 the projections of C_i on Ω from P as vertex of projection are coplanar. In this case, the generators g_1, g_2 of Ω at P and the lines joining P to the vertices C_i of Δ_1 all lie on a quadric cone of vertex P and hence g_1 and g_2 both belong to the same tetrahedral complex Γ whose fundamental tetrahedron is Δ_1. Hence g_1, g_2 and the four lines of intersection of the faces of Δ_1 with the tangent plane p to Ω at P all touch a conic, *viz.*, the complex conic of Γ in the plane p. Reciprocating this result in regard to Ω we immediately see that g_1, g_2 and the lines joining P to the vertices S_i of Δ_2 all lie on a quadric cone of vertex P. Hence the projections of S_i from p on Ω are coplanar. Hence on π the inverses of P w.r.t. the circles S_i lie on a circle. Thus the first part of $(1\cdot1)$ is proved. As a particular case of $(1\cdot1)$, we have the theorem that if the centres of four circles C_i lie on a circle then the centres of the four circles S_i respectively orthogonal to sets of three chosen from C_i also lie on a circle. $(2\cdot1)$

3. Next, taking Δ_1 as the tetrahedron of reference let the homogeneous co-ordinates of points in S_3 be so chosen that the equation of the Absolute takes the form

$$\Omega \equiv a_{11}x_1^2 + \cdots + a_{44}x_4^2 + 2a_{12}x_1x_2 + \cdots = 0.$$

If two circles Σ, Σ' are inverses of one another in regard to a circle C it is known that in S_3, Σ, Σ' are collinear with C and separate harmonically C and the point of intersection of the line with the polar plane of C in regard to Ω. The use of this property shows that if X be a circle of co-ordinates x_i and X_i the four circles which are respectively the inverses of X w.r.t. C_i, then the co-ordinates of X_i are obtained from those of X by simply changing x_i into $x_i - \frac{1}{a_{ii}}\frac{\partial\Omega}{\partial x_i}$ and leaving the three other co-ordinates unaltered. The condition of coplanarity of the points X_i is then easily seen to be

$$\psi_1 \equiv \frac{a_{11}x_1}{p_1} + \cdots + \frac{a_{44}x_4}{p_4} - 2 = 0 \qquad (3\cdot1)$$

where

$$p_i = \frac{1}{2}\frac{\partial\Omega}{\partial x_i} \quad (i = 1, 2, 3, 4).$$

Hence the ∞^2 circles C on π which are such that the inverses of C w. r. t. C_i have a common orthogonal circle are represented in S_3 by the points of the quartic surface ψ_1. The surfaces ψ_1 and Ω intersect in an octavic curve Γ_1. From the definitions of ψ_1 and Ω it is evident that the points of Γ_1 represent points P on π which are such that the inverses of P w. r. t. the circles C_i lie

on a circle. The latter part of (1·1) follows immediately by projecting on π from a point of Ω.

4. Let $\psi_2 = 0$ be the quartic surface related to Δ_2 and Ω in the same way as $\psi_1 = 0$ is related to Δ_1 and Ω. In virtue of (1·1), ψ_1 and ψ_2 both intersect Ω in the same octavic curve Γ_1. They will therefore intersect in a further curve Γ_2 of degree eight. Now, from (3·1), it is readily seen that the four lines $x_i = 0, \frac{\partial \Omega}{\partial x_i} = 0$; *i.e.*, the four lines of intersection of the corresponding faces of Δ_1, Δ_2 are lines lying on the surface ψ_1. From symmetry it follows that these four lines lie also on ψ_2. Thus Γ_2 breaks up into these four lines and a quartic curve. From this (1·2) follows immediately by projecting from a point of Ω on π. The curves Γ_1, Γ_2 on π intersect in 64 points. Of these, sixteen are the projections of the intersections of Γ_2 with Ω. Omitting these, we have the result.

There are 48 circles Σ having the properties:

(*a*) the inverses of Σ w.r.t. C_i have a common orthogonal circle as also the inverses of Σ w.r.t. the circles S_i.

(*b*) the inverses of the centre of Σ w.r.t. C_i lie on a circle as also the inverses w.r.t. the circles S_i.

5. Let X be a circle of co-ordinates x_i, X_i the inverses of X w.r.t. the circles C_i. Then the co-ordinates of X_i are obtained as mentioned in (3). If the circles X_i have a common orthogonal circle Y of co-ordinates y_i, the points X_i lie on the polar plane of Y in regard to Ω. The analytical expression of this condition gives immediately

$$\frac{1}{a_{11}} \frac{\partial \Omega}{\partial x_1} \frac{\partial \Omega}{\partial y_1} = \frac{1}{a_{22}} \frac{\partial \Omega}{\partial x_2} \frac{\partial \Omega}{\partial y_2} = \cdots = \frac{1}{a_{44}} \frac{\partial \Omega}{\partial x_4} \frac{\partial \Omega}{\partial y_4}.$$

Now, let $D = |a_{ij}|$ be the discriminantal determinant of the equation $\Omega = 0$ and let a^{ij} be the co-factor of a_{ij} in D. Then $\frac{\partial \Omega}{\partial x_i}, \frac{\partial \Omega}{\partial y_i}$ may be considered as the system of homogeneous co-ordinates of X, Y referred to Δ_2, for which the equation of the quadric Ω takes the form

$$a^{11} x^2_1 + \cdots + 2\, a^{12}\, x_1\, x_2 + \cdots = 0.$$

Hence, referred to Δ_2, if the tangential equation to the Absolute Ω be $a_{11} l^2 + a_{22}\, m^2 + a_{33}\, n^2 + a_{44}\, p^2 + 2a_{12}\, l\, m + \cdots = 0$ the point co-ordinates x_i, y_i (referred to Δ_2) of the circles X, Y are connected by the equations.

$$x_i\, y_i = a_{ii} \qquad (i = 1, 2, 3, 4).$$

These equations evidently define the involutoric cubic transformation whose singular points are the vertices of Δ_2 and whose fixed points are the eight points

$$(\sqrt{a_{11}}, \pm \sqrt{a_{22}}, \pm \sqrt{a_{33}}, \pm \sqrt{a_{44}})$$

forming the vertices of two tetrahedra which, with Δ_2, form a desmic system. These eight points are known to represent the eight circles which cut the circles C_i at equal angles.§ Thus (1·3) is proved.

When the circles X_i do not have a common orthogonal circle, the tetrahedron whose vertices are X_i is evidently in perspective with Δ_1, the centre of perspective being X. In this case it may be verified that the transformation mentioned above, carries X into the pole, in regard to Ω, of the plane of perspective of the two tetrahedra. Interpreted in terms of circle geometry, this means that if C_i' are the inverses w.r.t. C_i of any circle Σ and S_i' the circles orthogonal to sets of three chosen from C_i', the transformation carries Σ into the circle Σ' where Σ' is the common member of the four coaxal systems S_i S_i' ; $(i = 1, 2, 3, 4)$.

6. We next proceed to establish the result (1·4) connected with the Miquel-Clifford configuration. It is well known that the locus of points P which are such that the feet of the perpendiculars from P on four lines l_i no three of which are concurrent and no two are parallel $(i = 1, 2, 3, 4)$ lie on a circle is the circular cubic Γ_3 passing through the eight points of the Miquel-Clifford configuration generated by the four lines. Hence if P be a point on Γ_3, the reflections of P about the four lines l_i lie on a circle. By inverting this result we see, since the inverse of a circular cubic is a bicircular quartic or a circular cubic according as the centre of inversion does not or does lie on the curve, that the locus of points P which are such that the inverses of P w.r.t. four concurrent circles C_i lie on a circle is a bicircular quartic or a circular cubic according as the centres of C_i do not or do lie on a circle. In either case the locus passes through the eight points of the Miquel-Clifford configuration generated by the four circles C_i.

7. Let C be the Miquel-Clifford configuration generated by four circles C_i concurrent at a point which we denote by the symbol ( ) ; let (ij) denote the intersection, other than ( ), of the circles C_i, C_j and let (ijk) denote the circle through (ij), (jk), (ki). Let Γ_{ij} be the locus, which has been seen to be a cyclic, of points whose inverses with respect to the four circles of C passing through (ij) are concyclic. Γ_{ij} is known to pass through the eight points of C and it is readily seen that the limiting points of the coaxal system defined by C_i and C_j are points on Γ_{ij} as also on $\Gamma_{(\ )}$. Thus the cyclics Γ_{ij}, $\Gamma_{(\ )}$ have in common 10 points besides the two nodes at the circular points at infinity. Hence Γ_{ij} and $\Gamma_{(\ )}$ coincide with one another. We, therefore, arrive at the result " If the inverses of a point P w.r.t. four

§ A. Narasinga Rao, " The Concepts of Turbine Geometry, " *Journ. Ind. Math Soc.*, 1938, **3**, No. 3.

concurrent circles C_i lie on a circle, then the inverses of P w.r.t. any concurrent tetrad of circles of the Miquel-Clifford configuration generated by the four circles lie on a circle ". Taking now a fifth circle through the point of concurrence of the four circles C_i, if the inverses of a point P w.r.t. the five circles lie on a circle, it is readily seen by repeated application of the previous result that the inverses of P w.r.t. every concurrent set of five circles of the configuration generated by the five circles are concyclic and generally we shall have the theorem (1·4). In particular, when P is the point at infinity we have the interesting theorem :

If the centres of n concurrent circles C_i lie on a circle then the centres of any other set of n concurrent circles of the Miquel-Clifford configuration generated by the circles C_i also lie on a circle. (7·1)

In fact if the inverses of a point P w.r.t. a set of n concurrent circles and therefore, by theorem (1·4), w. r. t. every set of n concurrent circles of the Miquel-Clifford configuration generated by the n circles lie on a circle, we may associate with each circle of the configuration, a point—namely the inverse of P w. r. t. that circle, and with each point of the configuration a circle—namely the circle which passes through the n points associated with the n circles passing through the point. It is readily seen that the 2^{n-1} points and the 2^{n-1} circles thus derived define another Miquel-Clifford configuration.

PIGMENTS OF COTTON FLOWERS

Part VI.* Methylation of Herbacetin

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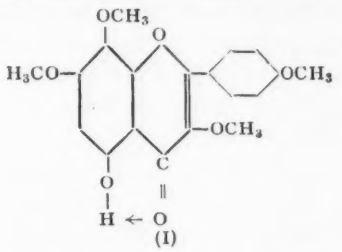
Herbacetin is a new flavonol which was isolated as its glucoside from the Indian cotton flowers[1] by Neelakantam and Seshadri who also established its constitution[2] as 3 : 5 : 7 : 8 : 4′-pentahydroxyflavone. It has been synthesised by Goldsworthy and Robinson.[3] The methylation of this substance by the ordinary methods using dimethyl sulphate or methyl iodide is difficult since it undergoes oxidation very readily in the presence of alkali and air. With diazomethane it is not completely methylated ; only a tetramethyl ether is formed which crystallises as a hydrate and loses the water of crystallisation (2 molecules) at about 120°. It is here described as 3 : 7 : 8 : 4′-tetramethylherbacetin since it is well known that position 5 is left unaffected by diazomethane. It is different from the isomeric ether, 3 : 5 : 8 : 4′-tetramethylherbacetin prepared by Goldsworthy and Robinson[3] in the course of their synthesis of herbacetin. The melting points and colour reactions are quite different. It is noteworthy that in the partially methylated flavonols a free hydroxyl group in position 5 does not markedly raise the melting point as compared with the completely methylated ethers whereas a free hydroxyl group in position 7 invariably raises the melting point considerably. This is obviously due to the effect of chelation between the carbonyl and the hydroxyl in the fifth position as in (I). The same effect accounts for the resistance to methylation offered by this position.



(I)

* The paper entitled "Constitution of Gossypitrin" published in this Journal, 1937, **6**, 12, is considered as Part V of this series.

Further methylation of 3 : 7 : 8 : 4′-tetramethylherbacetin with dimethyl sulphate and sodium hydroxide in aqueous acetone solution (Baker and Robinson's method[4]) yields pentamethylherbacetin. This compound also, like the tetramethyl ether, crystallises as a hydrate (3 molecules of water) and becomes anhydrous on drying at about 120°. In its reactions however it differs markedly from the tetramethylherbacetin. The anhydrous compound resembles closely in all its properties the sample of pentamethyl herbacetin obtained by Goldsworthy and Robinson by methylating 3 : 5 : 8 : 4′-tetramethylherbacetin with dimethyl sulphate and sodium hydroxide.

Experimental

3 : 7 : 8 : 4′-*Tetramethylherbacetin*.—Herbacetin (100 mg.) was dissolved in anhydrous methyl alcohol (25 c.c.) and treated at the room temperature (25°) with an ethereal solution of diazomethane (1 g.) in small quantities at a time. The solution became cherry red and the colour gradually disappeared. After leaving overnight, the ether was removed on a water-bath and more methyl alcohol was added. The liquid was then treated again with an ethereal solution of diazomethane (1 g.) in the above manner. After leaving overnight, the alcohol and ether were removed completely on a water-bath. On adding a few drops of water, a yellow sticky solid separated out. It was purified by crystallisation from aqueous alcohol twice (using a little animal charcoal) and finally from acetic acid. The tetramethyl ether was then obtained as yellow narrow rectangular plates which shrank and sintered from 120° to 125° (dehydration) and melted completely at 159–60°. (Found : Loss of H_2O, 9·0 ; C, 58·1 ; H, 5·8 ; OCH_3, 31·6 ; $C_{19}H_{18}O_7$, $2H_2O$ requires loss of H_2O, 9·1 ; C, 57·9 ; H, 5·6 ; OCH_3, 31·5%.) The substance easily lost all the water of crystallisation when kept at 120° for about two hours. The dehydrated sample melted at 160–62°. The hydrate lost one and a half molecules of water, when left in a vacuum desiccator for a day and the product contained only half a molecule of water. (Found : Loss of H_2O, 2·4 ; $C_{19}H_{18}O_7$, $\frac{1}{2}H_2O$ requires loss of H_2O, 2·5%.) The substance dissolved in concentrated hydrochloric acid or sodium hydroxide forming a yellow solution. Ferric chloride imparted a beautiful green colour to the substance in alcoholic solution.

3 : 5 : 7 : 8 : 4′-*Pentamethylherbacetin*.—The tetramethyl compound (I) (50 mg.) was dissolved in 10 c.c. of acetone. Dimethyl sulphate (1 c.c.) and 20% aqueous sodium hydroxide (1 c.c.) were added to the solution. An orange colour developed immediately and faded away gradually on shaking. Further quantities of dimethyl sulphate (2·5 c.c.) and sodium hydroxide (2·5 c.c.) were added in small quantities alternately and the contents were

shaken vigorously after each addition. Subsequently the liquid was kept strongly alkaline by the gradual addition of 3 c.c. more of the 20% alkali. The contents were left overnight and then refluxed on a water-bath for an hour. The acetone present was then driven off on the water-bath. On cooling and diluting the liquid, a colourless fibrous solid separated out. It could be easily crystallised from aqueous alcohol using a little animal charcoal in the form of fibrous needles. The pentamethyl ether sintered from 98 to 100° (dehydration) and melted at 156–58°. This could be completely dehydrated at 120° as in the case of the tetramethyl ether. (Found : Loss of H_2O, 12·5 ; $C_{20}H_{20}O_7$, $3H_2O$ requires loss of H_2O, 12·8%.) The dehydrated specimen melted at 157–58° (Goldsworthy and Robinson gave the melting point as 156–58°) and the mixed melting point with the dehydrated tetramethyl ether was depressed and indefinite from 140 to 45°. (Found : in the dehydrated specimen OCH_3, 41·4 ; $C_{20}H_{20}O_7$ requires OCH_3, 41·7%.) As stated by the above authors, the substance dissolved in cold concentrated or hot dilute hydrochloric acid forming a yellow solution of the oxonium salt, produced crystalline precipitates with ferric chloride and platinic chloride solutions and adsorbed iodine from aqueous solutions.

Summary

The action of diazomethane on herbacetin yields 3 : 7 : 8 : 4′-tetramethylherbacetin. The pentamethyl ether is obtained by the further methylation of the above tetramethyl compound with dimethyl sulphate and sodium hydroxide in aqueous acetone medium.

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POTENTIAL SOLUTIONS NEAR AN ANGULAR POINT

By B. R. Seth

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It is generally believed that the velocity (or stress) in the case of an irrotational potential solution is zero or infinite at an angular point according as the corresponding angle is less or greater than π. But no general analytical demonstration is available even for two dimensional cases excepting the one given by Pearson[1] for the torsion of prisms. In this paper we shall shew that if πa be the angle,

(i) the velocity is zero if $a < 1$;

(ii) the velocity is in general infinite if $a > 1$;

(iii) the velocity is zero even in (ii) if the physical problem and the section are both symmetrical about the bisector of the angle. This has been generally overlooked by writers. What happens is that the re-entrant angle behaves like two angles less than π and hence the velocity becomes zero and not infinite.

The velocity potential which is a solution of Laplace's equation generally satisfies a boundary condition of the form

$$\left[\frac{\partial \phi}{\partial x} - \sum_{s=0}^{n} f_s\right] \cos(xv) + \left[\frac{\partial \phi}{\partial y} + \sum_{s=0}^{n} \chi_s\right] \cos(yv) = 0, \qquad (1)$$

where f_n and χ_n are homogeneous integral polynomials of the nth degree in x and y and v denotes the direction of the normal drawn to the boundary.

We can re-write (1) as

$$\frac{\partial \psi}{\partial s} = \left[\sum_{s=0}^{n} f_s\right] \cos(xv) - \left[\sum_{s=0}^{n} \chi_s\right] \cos(yv), \qquad (2)$$

where s is measured along the boundary.

For fixed boundaries all f's and χ's vanish ; for a uniform motion of translation f_0 and χ_0 are only present ; for a motion of rotation and for certain viscous motions f_1 and χ_1, and for Saint-Venant's flexure problem f_2 and χ_2 also have to be taken.

[1] Todhunter and Pearson, *History of Elasticity*, Vol. II, Part II, pp. 412–14.

Let us solve the corresponding problem for a circular sector given by $\theta = \pm \frac{1}{2}\pi a, r = c$.

Along $\theta = \pm \frac{1}{2}\pi a$ (2) gives

$$\frac{\partial \psi}{\partial r} = \sum_{s=0}^{n} (A_s \pm B_s) r^s, \tag{3}$$

A's and B's being known constants and s integral.

We can satisfy (3) if we take

$$\psi = \sum_{s=0}^{n} \frac{r^{s+1}}{s+1} \left[A_s \frac{\cos (s+1)\theta}{\cos \frac{1}{2}(s+1)\pi a} + B_s \frac{\sin (s+1)\theta}{\sin \frac{1}{2}(s+1)\pi a} \right] + \psi_1, \tag{4}$$

where ψ_1 is such a solution of Laplace's equation that

$$\frac{\partial \psi_1}{\partial r} = 0 \text{ over } \theta = \pm \tfrac{1}{2}\pi a.$$

Since $-\frac{1}{2}\pi a \leqslant \theta \leqslant \frac{1}{2}\pi a$ the most general form ψ_1 can have is

$$\psi_1 = \sum_{s=0}^{\infty} \left[F_s \left(\frac{r}{c}\right)^{2s/a} \sin \frac{2s\theta}{a} + E_s \left(\frac{r}{c}\right)^{(2s+1)/a} \cos \frac{(2s+1)\theta}{a} \right], \tag{5}$$

where F_s and E_s are as yet undetermined constants.

Along $r = c$ (2) gives

$\frac{\psi}{\theta}$ = a known function of θ which can be expanded in a Fourier's series.

$$= \sum_{s=0}^{n} c^{s+2} \left[A_s \frac{\sin (s+1)\theta}{\cos \frac{1}{2}(s+1)\pi a} - B_s \frac{\cos (s+1)\theta}{\sin \frac{1}{2}(s+1)\pi a} \right]$$

$$- \sum_{s=0}^{\infty} \left[\frac{2s}{a} F_s \cos \frac{2s\theta}{a} - \frac{(2s+1)}{a} E_s \sin \frac{(2s+1)\theta}{a} \right]. \tag{6}$$

Comparing the co-efficients on both sides we get the values of F_s and E_s. The corresponding value of $\phi + i\psi$ is now given by [2]

$$\phi + i\psi = \sum_{s=0}^{n} L_{s+1} z^{s+1} + \sum_{s=0}^{\infty} F_s z^{2s/a} + i \sum_{s=0}^{\infty} E_s z^{(2s+1)/a}, \tag{7}$$

which shows that in general the velocity

$$q = \left| \frac{d}{dz} (\phi + i\psi) \right|$$

[2] It can happen that an E_s or a F_s may become infinite for some value of a. In such a case a L_s must also become infinite. Combining these two terms we get a term of the type $z^s \log z$, s being a positive integer. The velocity corresponding to this term is always zero at $z = 0$.

will contain a term of the type $r^{1/a-1} f(\theta)$, and hence it will be zero or infinite when r approaches zero according as

$$a < \text{or} > 1.$$

When both the section and the physical conditions are symmetrical about the bisector of the angle ψ must be odd in θ, and hence A_s and E_s must both vanish. In such a case (7) shows that the velocity is always zero.

We may look upon the problem in the following manner as well. In the boundary condition (1) ν, the direction of the normal is defined at all points except at an angular point where it can be anything. Hence at an angular point the co-efficients of both cos $(x\nu)$ and cos $(y\nu)$ should separately either vanish or become infinite. But this does not give the criterion to distinguish between the two cases.

ON A PROBLEM RELATED TO THE CAUCHY-MACLAURIN INTEGRAL TEST

By K. S. K. Iyengar

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1. Given : $f(x) > 0$ and $f(x) \to 0$ as $x \to \infty$; $f'(x) \leqslant 0$, $f''(x) \geqslant 0$; let $r(x)$ be defined by $r(x) = \sum_{n=0}^{\infty} \left\{ \int_{x+n}^{x+n+1} f(t)\,dt - f(x+n+1) \right\}$. It is the purpose of this note to discuss the behaviour of $\frac{r(x)}{f(x)}$ and its relation to the value of $\frac{f'(x)}{f(x)}$ for large x.

2. Theorem I : $\frac{1}{2} f(x+1) \leqslant r(x) \leqslant \frac{1}{2} f(x)$.

Since $f''(x) \geqslant 0$, for $x \leqslant t \leqslant x+1$ we shall have

$$\frac{f(x+1) - f(x)}{1} \leqslant \frac{f(t) - f(x+1)}{t - (x+1)} \leqslant \frac{f(x+2) - f(x+1)}{+1}$$

$$\therefore \quad \int_x^{x+1} \{f(t) - f(x+1)\}\,dt \leqslant [f(x) - f(x+1)] \int_x^{x+1} (x+1-t)\,dt$$

$$= \tfrac{1}{2} \{f(x) - f(x+1)\},$$

and similarly $\int_x^{x+1} \{f(t) - f(x+1)\}\,dt \geqslant \tfrac{1}{2} \{f(x+1) - f(x+2)\}$.

Therefore, $$\tfrac{1}{2} f(x) \geqslant r(x) \geqslant \tfrac{1}{2} f(x+1) \qquad \text{(A)}$$

Corollary : $\sum^{\infty} r(x+n)$ and $\sum^{\infty} f(x+n)$ converge or diverge together.

3. Theorem II : Besides the assumptions on $f(x)$ given above, let $\frac{f'}{f} \to -\theta \quad (\theta > 0)$.

Then, $$\frac{r(x)}{f(x)} \to \frac{1}{\theta} - \frac{1}{e^{\theta} - 1} = \lambda, \text{ say, as } x \to \infty$$

Proof: Since $\frac{f'}{f} \to -\theta$ as $x \to \infty$, $\dfrac{\int_x^{x+1} f(t)\,dt}{-\int_x^{x+1} f'(t)\,dt} = \dfrac{\int_x^{x+1} f(t)\,dt}{f(x) - f(x+1)}$

$$= \frac{1}{\theta + \epsilon}$$

and

$$\frac{f(x+1)}{f(x)} = e^{-(\theta + \epsilon')}, \text{ so that } \frac{f(x+1)}{f(x) - f(x+1)} = \frac{1}{e^{\theta + \epsilon'} - 1}.$$

Hence

$$\frac{\int_x^{x+1} f(t)\,dt - f(x+1)}{f(x) - f(x+1)} = \frac{1}{\theta+\epsilon} - \frac{1}{e^{\theta+\epsilon'}-1} = \frac{1}{\theta} - \frac{1}{e^{\theta}-1} + \epsilon_x'' \qquad \text{(B)}$$

$$\therefore \quad r(x) = \sum_{n=0}^{\infty} \left\{ \int_{x+n}^{x+n+1} f(t)\,dt - f(x+n+1) \right\}$$

$$= \sum_{n=0}^{\infty} (\lambda + \epsilon''_{x+n}) \{ f(x+n) - f(x+n+1) \}$$

$$= (\lambda + \epsilon_x''')\, f(x)$$

whence $$\frac{r(x)}{f(x)} \to \lambda \text{ as } x \to \infty.$$

If $\theta = 0$, $\quad \dfrac{f(x+1)}{f(x)} \to 1$ as $x \to \infty$,

Hence from (A), $\quad \dfrac{r(x)}{f(x)} \to \frac{1}{2}$ as $x \to \infty$.

If $\theta = \infty$, it is obvious from (B) that $\dfrac{r(x)}{f(x)} \to 0$ as $x \to \infty$.

4. *The Converse of Theorem II ; an inequality.*

Suppose it is given that $\dfrac{r(x)}{f(x)} \to \lambda$ as $x \to \infty$, where $0 \leqslant \lambda \leqslant \frac{1}{2}$, the assumptions on f, f' and f'' being the same as in § (1),

then $$r(x) - r(x+1) = \int_x^{x+1} f(t)\,dt - f(x+1) = \lambda \{ f(x) - f(x+1) \}$$

$$+ \epsilon_x f(x) - \epsilon_{x+1} f(x+1).$$

Now, since $f''(x) \geqslant 0$,

$$f(x+\tfrac{1}{2}) \leqslant \int_x^{x+1} f(t)\,dt = \lambda f(x) + \mu f(x+1) + \epsilon_x f(x) - \epsilon_{x+1} f(x+1)$$

$$\therefore \quad f(x+\tfrac{1}{2}) - f(x+1) \leqslant \lambda \{ f(x) - f(x+1) \} + \epsilon_x f(x) - \epsilon_{x+1} f(x+1)$$

$$f(x+1) - f(x+\tfrac{3}{2}) \leqslant \lambda \{ f(x+\tfrac{1}{2}) - f(x+\tfrac{3}{2}) \} + \epsilon_{x+\frac{1}{2}} f(x+\tfrac{1}{2})$$

$$- \epsilon_{x+} \quad f(x+\tfrac{3}{2})$$

$$\cdots\cdots\cdots\cdots, \text{ etc.}$$

Hence $$f(x+\tfrac{1}{2}) \leqslant \lambda \{ f(x) + f(x+\tfrac{1}{2}) \} + \epsilon_x f(x) + \epsilon_{x+\frac{1}{2}} f(x+\tfrac{1}{2})$$

and $$f(x+\tfrac{1}{2}) \leqslant \left(\frac{\lambda}{\mu} + \epsilon_x' \right) f(x). \qquad \text{(C)}$$

Assume $\lambda \neq 0$. Then, since $f''(x) \geqslant 0$, if A is $\{x, f(x)\}$, Pis $\{x+\lambda, f(x+\lambda)\}$ and B is $\{x+1, f(x+1)\}$, the curve composed of the chords AP, PB lies above the curve $y = f(x)$.

Hence $\lambda \cdot \dfrac{f(x)+f(x+\lambda)}{2} + \mu \dfrac{f(x+\lambda)+f(x+1)}{2} \geqslant \int_x^{x+1} f(t)\,dt$

$$= \lambda f(x) + \mu f(x+1) + \epsilon_x f(x) - \epsilon_{x+1} f(x+1)$$

$$\therefore \quad f(x+\lambda) \geqslant \lambda f(x) + \mu f(x+1) + 2\,\epsilon_x f(x) - 2\,\epsilon_{x+1} f(x+1) \qquad \text{(D)}$$

Also $$f(x+\lambda) \geqslant (\lambda - \epsilon) f(x)$$

and $$\frac{f(x+1)}{f(x)} \geqslant (\lambda - \epsilon)^{\left[\frac{1}{\lambda}\right]+1} = \lambda^{\left[\frac{1}{\lambda}\right]+1} - \epsilon' = K_\lambda - \epsilon$$

Hence, when $\lambda \neq 0$,

$$\left(\frac{\lambda}{\mu}\right)^2 + \epsilon' \geqslant \frac{f(x+1)}{f(x)} \geqslant K_\lambda - \epsilon \qquad \text{(E)}$$

From this it is easy to deduce that $-\dfrac{f'}{f}$ oscillates, if at all, finitely, between two positive values for large x. There are two interesting cases when $\lambda = 0$ and $\lambda = \frac{1}{2}$, where we can prove that $\dfrac{f'}{f}$ definitely converges as $x \to \infty$.

THEOREM III : *If, as* $x \to \infty$, $\dfrac{r(x)}{f(x)} \to 0$, *then* $\dfrac{-f'}{f} \to \infty$, *and if* $\dfrac{r(x)}{f(x)} \to \frac{1}{2}$ *then* $\dfrac{-f'}{f} \to 0$ (*under the same assumptions about* f, f' *and* f'' *as before*).

Proof : (i) $\lambda = 0$.

From (C) or (A), $$\frac{f(x+1)}{f(x)} = \epsilon_x$$

$$\therefore \quad r(x) = \int_x^\infty f(t)\,dt - \sum_{n=1}^\infty f(x+n) = \int_x^\infty f(t)\,dt - \epsilon_x' f(x)$$

therefore $$\int_x^\infty f(t)\,dt = \epsilon_x'' f(x).$$

Now the area between the X-axis, the lines $\bar{X} = x$ and the tangent $\bar{Y} - f(x) = f'(x)(\bar{X} - x)$

is $$-\frac{f^2(x)}{2f'(x)} < \int_x^\infty f(t)\,dt = \epsilon_x''\, f(x).$$

Hence $$\frac{f}{f'} \to 0, \text{ as } x \to \infty.$$

(ii) $\lambda = \frac{1}{2}$.

From (D) we have

$$f(x+\tfrac{1}{2}) \geqslant \tfrac{1}{2}\{f(x) + f(x+1)\} + 2\,\epsilon_x f(x) - 2\,\epsilon_{x+1} f(x+1)$$

$$f(x+1) \geqslant \tfrac{1}{2}\{f(x+\tfrac{1}{2}) + f(x+\tfrac{3}{2})\} + 2\,\epsilon_{x+\frac{1}{2}} f(x+\tfrac{1}{2}) - 2\,\epsilon_{x+\frac{3}{2}} f(x+\tfrac{3}{2})$$

$$\cdots\cdots\cdots, \text{ etc.}$$

Writing these in the form

$f(x+\frac{1}{2}) - \frac{1}{2}\{f(x) + f(x+1)\} \geqslant 2\,\epsilon_x f(x) - 2\,\epsilon_{x+1} f(x+1)$, etc.

and adding, we get $-\{f(x) - f(x+\frac{1}{2})\} \geqslant 4\{\epsilon_x f(x) + \epsilon_{x+\frac{1}{2}} f(x+\frac{1}{2})\}$

[It is to be noticed that, from (A), all the ϵ's are negative.]

Hence $$\epsilon_x' \geqslant \frac{f(x) - f(x+\frac{1}{2})}{f(x)} \geqslant 0$$

i.e., $$\frac{f(x+\frac{1}{2})}{f(x)} \to 1 \quad \text{as } x \to \infty.$$

Also $$2\epsilon_x' \geqslant \left\{\frac{f_0(x) - f(x+\frac{1}{2})}{\frac{1}{2}f(x)}\right\} = \frac{-f'\left(x+\frac{\theta}{2}\right)}{f(x)} \geqslant \frac{-f'(x+\frac{1}{2})}{f(x)}$$

$$= \frac{-f'(x+\frac{1}{2})}{f(x+\frac{1}{2})}(1+\varepsilon_x).$$

Hence $$\frac{-f'}{f} \to 0 \text{ as } x \to \infty.$$

5. The problem of the asymptotic behaviour of $\frac{f'}{f}$ when $\frac{r(x)}{f(x)} \to \lambda$, as $x \to \infty$, has been partially solved in § 4. It has been there shown that, in two particular cases, *viz.*, $\lambda = 0$ and $\lambda = \frac{1}{2}$, the behaviour of $\frac{f'}{f}$ is definite. This raises the interesting problem : *Under the restrictions on $f(x)$ given above, let $\frac{r(x)}{f(x)} \to \lambda$, as $x \to \infty$, where $0 < \lambda < \frac{1}{2}$. Then, does $\frac{f'}{f}$ necessarily tend to a definite limit as $x \to \infty$?*

STUDIES IN THE PROPERTIES OF BIVALENT METAL OLEATES—PART I

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The heavy metal salts of the higher fatty acids, owing to their application in art, have been known for a long time. These metallic soaps are particularly interesting not only because of their industrial importance but also from purely theoretical considerations.

It has been pointed out by Lewkowitsch[1] and Bhatnagar[2] that the bi- and tri-valent soaps are not simple chemical compounds, but are complex adsorption compounds and their composition varies considerably with the amount of monovalent soap and the precipitating electrolyte used. McBain, Winfred and McClatchie[3] observed that aluminium oleate contained 5·0 to 6·2 per cent. of aluminium. This indicates a composition slightly nearer the dibasic rather than the monobasic soap, showing that aluminium soaps are commonly a mixture of uncombined free acid with either a monobasic or a mixture of mono- and di-basic soaps. Normal tribasic aluminium soaps have never been prepared even in the anhydrous media. Winkler[4] found that magnesium salts require more alkali soap than an equivalent amount of calcium salts. Master and Smith[5] observed that magnesium oleate carried down with it sodium oleate from solution. Recently Ostwald and Riedel[6] have found that aluminium soaps of propionic, butyric, valeric, lauric, palmitic, oleic and stearic acids contain 1·1–1·6 atoms of the element per three mols of the fatty acid.

Different views have been put forward to account for the discrepancies observed in the composition of the metal soaps. Bhatnagar[7] suggested that it was due to the adsorption of ions which would be formed due to dissociation or hydrolysis of the electrolyte and the monovalent soap. Cady[8] advocated that it was due to the oxide formation within the metallic soap. To investigate this point different samples of zinc and magnesium oleates

were prepared by varying the amount of components and their physical properties such as solubility, molecular complexity, viscosity, surface tension, conductivity and magneto-optical rotation, were studied.

Experimental

Preparation of the Oleates.—The bivalent salts of oleic acid were prepared by the interaction of bivalent electrolytes and the solution of pure sodium oleate prepared according to the method of McBain.[9] Equimolecular quantities of sodium oleate and metal sulphate were taken. Sodium oleate was dissolved in hot water. The warm solution of the sodium soap was poured, while stirring, into the pure metal sulphate solution. If the amount of electrolyte was less than the molecular quantity, a colloidal solution was obtained which passed through the filter-paper. The electrolyte was, therefore, added in slight excess so as to get a flocculent white precipitate of the metal oleate. This was filtered, washed till free from the sulphate ions. The solid mass was pressed under filter-paper, washed with acetone and dried at 70–80° C. till the weight was constant. This was semi-solid when hot, but on cooling gave a white mass, which could be powdered in the case of zinc oleate and a semi-transparent yellow mass in the case of magnesium oleate. The samples were kept in a vacuum desiccator over calcium chloride or phosphorus pentoxide till further use. The composition of the metal soaps was determined from the oxide left after the ignition of the oleates.

Different samples of oleates were prepared by varying the amounts of components, and the effect of these on the composition of the oleate formed was studied. The metal oleates from colloidal solutions were obtained as coagula by centrifuging. Besides these samples, another sample of zinc oleate was prepared by refluxing zinc dust and oleic acid for about two hours at 130–40° C. This was filtered when hot. On cooling, a semi-solid mass separated which was treated several times with ether till a creamy white mass was obtained. It was kept in a vacuum desiccator till further use.

It was found on analysis that zinc and magnesium oleates obtained from solutions with excess of the electrolyte contained for every atom of zinc 1·95 molecules of oleic acid and for every atom of magnesium 1·80 molecules of oleic acid. The results obtained are recorded in Table I.

Theoretically, for every atom of metal two molecules of the acid should be present. From the analysis it is clear that the metal and the acid are not present in stoichiometric ratios. Similar observations were made by Ostwald and Riedel,[6] who found that in magnesium palmitate and stearate

TABLE I

Sample	% of Metal	Composition	
		Metal	Acid
1. Zinc oleate (when electrolyte is in excess) ..	10·64	1·0	1·95
2. Zinc oleate from zinc dust	10·42	1·0	2·00
3. Zinc oleate (when equi-molecular quantities are mixed)	10·34	1·0	2·02
4. Zinc oleate (when sodium oleate is in excess)	10·20	1·0	2·05
5. Magnesium oleate (when electrolyte is in excess)	4·34	1·0	1·80
6. Magnesium oleate (when equimolecular quantities are mixed)	3·80	1·0	2·04
7. Magnesium oleate (when sodium oleate is in excess)	3·65	1·0	2·12

the ratio of the metal to the acid was 1·90 and 1·88, respectively. The deviation from the theoretical value, as is clear from the above table, may be due to the adsorption of various ions which would have been formed due to the hydrolysis or dissociation of the electrolyte. It was observed, however, that in presence of excess of sodium oleate the metal oleate did not separate out but remained as a colloidal suspension. The colloidal particles were found to be negatively charged. When the amount of the electrolyte was increased the precipitate started settling out and was found to be positively charged. It was further observed that the pH of the solution changed from 8·5 to 5·9 as the amount of magnesium sulphate was increased to precipitate magnesium oleate from the colloidal solution. As long as the solution remained alkaline the metal oleate remained in the colloidal state, but as soon as the solution became acidic the soap started precipitating out. It suggests, therefore, that when sodium oleate is in excess the oleate micelle are adsorbed by the metal oleate particles and form a negatively charged colloidal solution, but when magnesium ions are in excess they are adsorbed and coagulate the metal oleate as a positively charged precipitate. If that be so, then the metal oleate containing excess of electrolyte should contain a greater percentage of the metal than the theoretical value. This is in agreement with the results shown in Table I.

The melting points of all the samples prepared were determined and are given below :—

TABLE II

Samples	Nature	m.p.
1. Zinc oleate (when electrolyte is in excess)	Yellowish white powder	78·0° C.
2. Zinc oleate from zinc dust	Creamy white powder	85·5° C.
3. Zinc oleate (when sodium oleate is in excess)	Yellowish white sticky mass	78·8° C.
4. Zinc oleate (when equimolecular quantities are mixed)	Yellowish white powder	85·1° C.
5. Magnesium oleate (when electrolyte is in excess)	Yellow, transparent, can be powdered	70–75° C.
6. Magnesium oleate (when equimolecular quantities are mixed)	Yellow mass	No definite m.p.
7. Magnesium oleate (when sodium oleate is in excess)	Yellow gummy	

From the results recorded above, it is clear that pure zinc oleate is a white powder with m.p. 85·5° C. and the other samples obtained by varying the amounts of components are yellowish white with m.p. varying from 78·0–85·1° C. Similarly magnesium oleate (pure) is a yellow mass which can be powdered, while the other samples are sticky. All the samples melt over a range 60–75° C. The difference in nature and the lowering in the m.p. of different samples of metal oleates can only be ascribed to the presence of different amounts of adsorbed ions as impurities in them.

Solubility.—The importance of solubility determination of metallic soaps is evident from the remarks which appear in *Technology of Oils, Fats and Waxes* by Lewkowitsch, 1921 Edition. The editor points out that a research on the solubility of these salts in organic solvents will be useful not only for a chemist interested in the chemistry of soaps, but also for those studying the chemistry of fatty acids, especially as regards their identification and separation from one another. The importance is twofold : (i) theoretical and (ii) technical. At present there is no suitable method

which can be applied by an analyst for separating the fatty acids, and it has been suggested that by knowing the solubilities of the various bi- and trivalent salts of these fatty acids in various solvents, their separation and identification would be possible. A knowledge of the solubility of these salts is also useful, if not essential, for those interested in the chemistry of paints and varnishes. Bhatnagar, while studying the nature and properties of emulsifying agents, found that barium oleate, calcium and zinc stearates are practically insoluble in benzene and turpentine oil at 20° C. Some of the heavy metal soaps are soluble in alcohol, some in ether and others in benzene and no general regularity was observed regarding their solubility.

Solubilities of magnesium and zinc oleates in benzene were determined at 20° and 60° C. Because of the volatility of benzene, special apparatus as shown in Fig. 1 was constructed. After crushing to a fine powder, a sufficient quantity of the soap to be examined was put in bottle A with

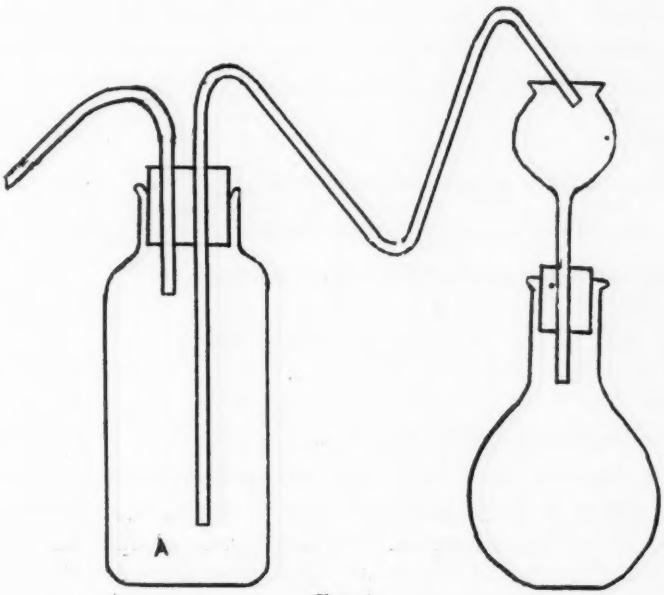

FIG. 1

about 100 c.c. of benzene and the two were shaken vigorously for an hour and the bottle A was then corked and left overnight in a thermostat at 20°. The solubility in hot benzene was determined by placing the bottle A in a bath at 60° C. The ordinary cork was then replaced by a double-bored cork carrying the two tubes, one with a long stem dipping right into the

clear portion of the solution and the other a shorter one, used for blowing the clear solution, to a wide-mouthed funnel fixed on a carefully cleaned flask by a water-tight stopper. The solution was thus blown over, while the flasks were dipping in the thermostat. When about 75 c.c. of the clear solution had been filtered, a weighed portion of it was taken out on three watch glasses of known weights and evaporated to constant weight. From the increase in weight the solubility was determined. The results obtained are tabulated below.

TABLE III

Solubility of Zinc and Magnesium Oleates in Benzene

Samples	Solubility	
	at 20°	at 60°
1. Zinc oleate from zinc dust	0·50	5·0
2. Zinc oleate (when the electrolyte is in excess) : freshly prepared	8·50	12·5
aged	2·06	..
3. Zinc oleate (when equimolecular quantities are mixed)	2·30	12·0
4. Zinc oleate (when sodium oleate is in excess) ..	2·05	12·0
5. Magnesium oleate (when equimolecular quantities are mixed)	2·20	12·0
6. Magnesium oleate (when electrolyte is in excess): freshly prepared	9·20	13·5
aged	2·15	
7. Magnesium oleate (when sodium oleate is in excess) ..	2·00	11·9

The difference in the solubilities may be due to the presence of complexes formed by the adsorption of different ions. Copper oleate obtained by Cady[8] was more soluble than that obtained by Kahlenberg.[10] The difference in the solubility and other properties was attributed to the formation of basic salts in the samples prepared by Cady from sodium oleate containing an excess of alkali. From the results obtained it is clear that zinc and magnesium oleates obtained from solutions containing the electrolyte in excess are more soluble than the pure samples, suggesting the formation of complex salts as postulated by Cady.

It was also observed that freshly prepared samples of metal oleates are more soluble than those which have been kept for some time. It seems probable that the metal oleates, on ageing, decompose and form metal oxide -oleic acid complexes which are less soluble.

Molecular Complexity.—Compounds dissolve in benzene, either as single or associated molecules. Association was observed by Meisenheimer[11] in a large number of organic substances representing many different types of compounds, when dissolved in benzene. He further concluded that as a general rule the degree of association increases linearly with the concentration of the solution. Recently Staudinger and Trommsdroff[12] showed that esters of poly-acrylic acid are associated in benzene from 2 to 5000 molecules.

Attempts were made to investigate the complexity of these metal oleates in benzene by determining their molecular weight in benzene. The usual technique of the Beckmann cryoscopic method was followed, the solid being introduced into pure benzene. But the depression in the freezing point produced in benzene on the addition of oleate was negligible.

TABLE IV

Depression Constant $K = 49 \cdot 8$

Samples	Weight of oleate gm.	Weight of camphor gm.	Depression	Molecular Weight
1. Zinc oleate from zinc dust ..	0·0208	0·2814	5·70°	645·90
2. Zinc oleate (when sodium oleate is in excess)	0·0326	0·3996	6·34°	644·8
3. Zinc oleate (when electrolyte is in excess)	0·0320	0·4001	6·20°	642·2
4. Magnesium oleate (when equimolecular quantities are mixed)	0·0178	0·4344	1·70°	1200·0
5. Magnesium oleate (when sodium oleate is in excess) ..	0·0300	0·2914	4·30°	1192·0
6. Magnesium oleate (when electrolyte is in excess) ..	0·1164	0·6350	7·4°	1234·0

As zinc and magnesium oleates do not depress the freezing point of benzene, it follows that true solutions are not formed. It has already been pointed out by Ostwald and Riedel[6] that these metal oleates are colloidal in nature. It is very difficult to determine the molecular weights of colloidal solutions as is evident from McBain's investigations,[13] who found that the boiling point and the vapour pressure methods gave erroneous results. The complexity of the molecules was, however, investigated by studying the depression of the melting point of camphor by Rast's method.[14]

The molecular weight for magnesium oleate should be 587·06 and for zinc oleate 628·11, but from the results obtained by the Rast method it looks as if magnesium oleate is doubly associated in camphor.

Viscosity.—The viscosity of zinc and magnesium oleates in benzene was determined using an Ostwald viscometer. The results obtained are recorded below :

TABLE V

Zinc Oleate in Benzene

Time of flow for water = 250 seconds

Temperature = 17·5° C.

No.	% of Oleate	Time of flow in seconds	Density	Relative viscosity	Viscosity as compared with benzene as unity
1	0·00	179·5	0·8720	0·6839	1·0000
2	2·19	193·2	0·8745	0·7381	1·079
3	3·42	197·2	0·8750	0·7538	1·103
4	3·48	198·2	0·8753	0·7578	1·109
5	4·26	203·5	0·8759	0·7788	1·139
6	5·27	209·5	0·8765	0·8023	1·172
7	6·41	216·0	0·8779	0·8285	1·212
8	8·50	221·0	0·8790	0·8492	1·242

TABLE VI

Magnesium Oleate in Benzene

Temperature = 17·5° C.

No.	% of Oleate	Time of flow in seconds	Density	Relative viscosity	Viscosity as compared with benzene as unity
1	0·00	179·5	0·8720	0·6839	1·000
2	1·38	190·0	0·8748	0·7263	1·062
3	2·01	195·0	0·8755	0·7457	1·087
4	2·17	196·1	0·8763	0·7508	1·097
5	3·13	202·0	0·8770	0·7742	1·132
6	4·22	206·5	0·8771	0·7914	1·158
7	4·30	207·1	0·8771	0·7936	1·161
8	5·49	215·9	0·8780	0·8281	1·211
9	5·80	216·5	0·8785	0·8310	1·215
10	6·01	217·6	0·8788	0·8356	1·222
11	7·00	220·4	0·8800	0·8474	1·239
12	7·90	223·5	0·8828	0·8602	1·259

From the results it is clear that the viscosity increases linearly with the increase in concentration and for the same concentration magnesium oleate in benzene produces a more viscous solution than the zinc oleate.

Ostwald and Riedel,[6] while studying the viscosity of metal soaps in benzene, observed that viscosity varied linearly with concentration. The concentration-viscosity curve tended to be less steep with an increase in the molecular weight of the acid of the metal soaps. They further concluded that soaps could not be treated as colloidal electrolytes but behaved more like gels. In the case of magnesium and zinc oleates studied, though the molecular weight of the acid is the same, yet for the same concentration the former oleate is more viscous. Therefore, the greater viscosity of magnesium oleate suggests some structural difference between zinc and magnesium oleates.

Surface Tension.—Oleates of the alkali metals when dissovled in water lower its surface tension to a considerable extent, and are largely used as emulsifying agents. The surface tension of zinc and magnesium oleates, when dissolved in benzene, was determined by the drop weight method. The results are embodied in Tables VII and VIII. The interfacial tension

TABLE VII

Zinc Oleate in Benzene

Temperature = 22·0° C.

No.	% of Oleate	Weight of one drop of solution in gm.	Surface tension in dynes/cm.
1	0·00	0·03101	28·55
2	2·12	0·03097	28·51
3	4·54	0·03096	28·50
4	5·27	0·03096	28·50
5	6·40	0·03096	28·50
6	6·91	0·03095	28·49
7	8·10	0·03092	28·46
8	8·50	0·03092	28·46

TABLE VIII

Magnesium Oleate in Benzene

Temperature = 22·0° C.

1	1·38	0·03098	28·52
2	2·01	0·03096	28·50
3	3·32	0·03095	28·49
4	4·22	0·03094	28·49
5	5·80	0·03094	28·48
6	7·20	0·03093	28·47
7	7·90	0·03091	28·45

benzene-water was determined by the drop number method and the results are given in Tables IX and X in which the first column gives the concen-

TABLE IX

Interfacial Tension Benzene-Water
Zinc Oleate in Benzene

Temperature = 22° C.

No.	% of Oleate	Drop numbers	Relative tension
1	0·00	22·0	1·0000
2	2·12	24·0	0·9166
3	3·42	25·5	0·8628
4	4·54	26·0	0·8461
5	5·27	26·5	0·8303
6	6·41	28·0	0·7856
7	6·91	28·25	0·7787
8	8·10	29·5	0·7457
9	8·50	30·0	0·7333

TABLE X

Magnesium Oleate in Benzene

1	0·00	22·0	1·0000
2	0·76	26·5	0·8303
3	1·38	30·0	0·7333
4	2·01	34·0	0·6471
5	3·13	40·0	0·5499
6	4·22	46·0	0·4782
7	5·80	55·0	0·3999
8	7·00	64·0	0·3438
9	7·90	69·0	0·3188

tration of the solution, the second the corresponding drop numbers which are inversely proportional to tension, and the third column gives the relative tension.

The lowering in air-benzene tension by the presence of oleate in benzene is very little. If, however, the interfacial tension between the oleate solutions in benzene and water is examined (Tables IX and X), the interfacial tension between water and benzene is found to be very much lowered by magnesium oleate, whereas it is effected to a comparatively small extent by zinc oleate. It was, however, observed that the lowering in benzene-water interfacial tension by the aged samples was less than that by freshly prepared ones. This difference in behaviour between an old and a fresh sample as has been suggested already from solubility considerations, seems to be due to the formation of a metal oxide oleic acid complex on standing. It has been found that magnesium oleate can be used as an emulsifying agent and forms a good emulsion of benzene and water whereas zinc oleate is not so good an emulsifying agent. Thus magnesium oleate resembles the alkali oleates in its emulsifying power and in its property of lowering the interfacial tension between water and benzene.

Conductivities in Benzene.—Previous data for the conductivity of salts in benzene is limited since these salts are as a rule not sufficiently soluble to give conducting solutions. Cady and Baldwin[15] while studying reactions in benzene found that silver melissinate, copper stearate, copper oleate and similar salts in benzene showed some conductivity which increased on passing dry hydrogen chloride. They further observed that the salts of unsaturated acids showed more conductivity and reacted more rapidly with hydrochloric acid than those of saturated ones. They attributed this to greater ionisation of the salts of unsaturated acids and their capacity to form addition compounds. Silver perchlorate is fairly soluble in benzene but gives non-conducting solutions. The thiohydrate of aluminium bromide, $AlBr_3 \cdot H_2S$ is soluble in benzene and its specific conductivity over the range 20–54 per cent. of salt has been shown by Jakubsohn[16] to rise to $3 \cdot 54 \times 10^{-4}$ ohm^{-1} for the most concentrated solution. Its molecular weight, as determined by the cryoscopic method, was observed, to increase with an increase in concentration. The change in the molar conductivity and the molecular weight with an increase in concentration therefore suggests that the formation of a greater number of conducting micelle is favoured by association.

The specific conductivity of the oleates in benzene was determined at 29° C. The oleates were dissolved in pure benzene (thiophene free) which had been dried for 3 to 4 weeks over sodium wire. The conductivity cell consisted of electrodes of platinum black about 5 mm. apart, and had contact

with mercury through the side tubes. The cell was guarded against evaporation by a tight glass stopper.

For the determination of conductivity the alternating current headphone method gave negative results. Therefore, the direct current method was resorted to.

The conductivity cell was connected to an Hartman and Braun galvanometer through a battery and a key. The other circuit was completed through a known resistance. The source of current was a large battery capable of giving constant E.M.F. upto 150 volts. The galvanometer, cell and the entire system were insulated by placing them on sulphur. The cell was cleaned and dried so thoroughly that when 110 volts was applied, the galvanometer showed no deflection. The benzene, which had been dried for a number of weeks, when put in the cell did not conduct any current. 7 Per cent. solution of zinc oleate in the same benzene was next introduced into the cell, but no deflection was observed even with 110 volts. When, however, a benzene solution of magnesium oleate was introduced into the conductivity cell, the deflection even with 40 volts was so great that the spot on the scale was thrown out. By knowing the resistance and the cell constant the specific conductivities were calculated for different concentrations of magnesium oleate and are given below.

TABLE XI

Conductivity of Magnesium Oleate in Benzene

Temperature = 29° C.
Cell Constant = 0·47

% of Oleate	Resistance of solution (ohms)	Specific conductivity (ohms)
1·40	10836363·30	$4·4140 \times 10^{-8}$
2·98	5256637·10	$0·8977 \times 10^{-7}$
4·90	2682727·28	$1·7390 \times 10^{-7}$
7·80	1330337·07	$3·5250 \times 10^{-7}$
9·10	1166262·30	$4·0300 \times 10^{-7}$

If conductivity be due to unsaturation as suggested by Cady and Baldwin, both zinc and magnesium oleates should be conducting, which is contrary to our observations. Association alone cannot account for the

conductivity of magnesium oleate because both zinc and magnesium oleates have been shown to be associated in benzene.

The peculiar behaviour of magnesium oleate in contra-distinction to zinc oleate in giving electrically conducting solutions in benzene is probably ascribable to its solvation leading to the formation of micelle and its consequent behaviour like a colloidal electrolyte. The presence of such micelle in a benzene solution of magnesium oleate is also indicated by the observation that magnesium oleate, in contrast to zinc oleate, lowers the interfacial tension between benzene and water to a considerable extent and can be used as a good emulsifying agent.

Magneto-optical Rotation.—From the above study of the various physical properties of zinc and magnesium oleates, it will be seen that magnesium oleate resembles more a colloidal electrolyte than a gel, whereas the behaviour of zinc oleate is more akin to a gel. This difference is probably due to the formation of ionic micelle when magnesium oleate is dissolved in benzene.

It has been shown that a study of the magneto-optical rotation of alkali soaps can furnish evidence as to the formation of ionic micelle.[17] Therefore, a study of magneto-optical rotation of zinc and magnesium oleates in benzene was carried out.

The molecular magnetic rotation was determined by the method described in a previous paper from this laboratory.[18] The results obtained are tabulated below :—

TABLE XII

Zinc Oleate in Benzene

Temperature = 19·5°C. Current = 9·4 amps.
Rotation for water = 7·69°
Molecular magnetic rotation of benzene = 11·27

No.	% of Oleate	Density of solution	Angle of rotation of solution	Molecular magnetic rotation
1	7·80	0·8782	16·85°	43·60
2	6·25	0·8778	16·98°	44·00
3	2·987	0·8748	17·215°	43·60
			(Mean)	43·70

TABLE XIII

Magnesium Oleate in Benzene

1	7·804	0·8827	16·74°	28·21
2	4·933	0·8774	16·95°	27·10
3	3·501	0·8770	17·11°	26·01
4	1·390	0·8748	17·31°	23·12

From the results it is clear that the molecular magnetic rotation of zinc oleate in benzene remains constant whereas that of magnesium oleate varies with the concentration. From the conductivity data it has been inferred that the conductivity of magnesium oleate is due to solvation and association of molecules, and the formation of micelle. The influence of concentration of colloidal electrolytes on molecular magnetic rotation has already been shown to be due to the formation of ionic micelle.[16] Therefore, the variation of the molecular magnetic rotation with changes in concentration of magnesium oleate supports the conclusion arrived at from a study of the other physical properties of the salt, *viz.*, a benzene solution of magnesium oleate contains ionic micelle.

Summary and Conclusions

Different samples of zinc and magnesium oleates were prepared by varying the amounts of the electrolyte and the monovalent soap. As a result of the analysis of the samples thus prepared, it is observed that the metal and the acid are not present in stoichiometric ratios except in the case of zinc oleate obtained by refluxing zinc dust and oleic acid. This sample of zinc oleate melts at 85·5° C. while the other samples melt at a much lower temperature. Similar behaviour is observed in the case of magnesium oleate. It has been suggested that these variations are due to the adsorption of various ions by the metal soaps formed.

A study of other physical properties such as solubility, molecular complexity, surface tension, viscosity, electric conductivity, and molecular magnetic rotation using benzene as solvent reveals that the behaviour of magnesium oleate is different from that of zinc oleate inasmuch as it shows conductivity, abnormally high molecular weight, comparatively higher viscosity, a greater lowering of interfacial tension and a variation of molecular magnetic rotation with change in concentration.

Riedel from a study of the viscosity of metal soaps concluded that these soaps could not be treated as colloidal electrolytes but that they behaved more like gels. The difference in behaviour of zinc and magnesium oleates, however, suggests that whereas zinc oleate may be regarded as a gel, magnesium oleate behaves more like a colloidal electrolyte.

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STUDIES IN TURBINE GEOMETRY—III* THE NON-ORIENTED LINE ELEMENT IN TWO-DIMENSIONAL MOBIUS GEOMETRY

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1. Sophus Lie obtained two representations of line elements in a plane by points in 3-space which have been shown[1] to be essentially representations of oriented line elements in a Euclidean plane, and of non-oriented elements in a minimal plane in such a manner that circles on the planes correspond to the lines of a linear complex. Representations of the manifold of line elements of a plane as binary-ternary,[2] double ternary[3] (in contragredient variables) and of oriented line elements of a sphere as triple binary[4] domains, and their representation in 3-space by projection from their associated Segre Manifolds have appeared in recent years. A fair idea of the work done in this field may be had from the " Geschitlische Entwicklung der Lehre von der Geraden-Kugel Transformation " by Prof. E. A. Weiss, whose own contributions to this region are not inconsiderable.

In this paper the main interest is not any scheme of analytic representation but the geometry of line elements under the extended point transformations of the inversive group. A representation free from singularities of the line element of the Mobius plane on a V_3^4 in a projective S_5, is obtained

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* The first two papers of this series are :

(I) " The Concepts of Turbine Geometry," *Jour. Ind. Math. Soc.*, New Series, **3**, 96–108.

(II) " On the Sub-geometries of Lie which belong to the Mobius Laguerre Pencil," *Proc. Ind. Acad. Sci.*, 1938, **8**, 179–86.

These will be referred to briefly as T.G. I and T.G. II.

[1] E. A. Weiss, " Die Geschictliche Entwicklung der Lehre von der Geraden-Kugel Transformation," *Deutsche Mathematik*, Jahrg. 3 S. 19. I have to thank Prof. Weiss for a set of reprints of his recent papers.

[2] E. A. Weiss, " Das Linienelement als singulare Punktreihe," *Jour. f.d. reine u. ange. Mathematik*, Bd. 117 (1937). This paper has several points of contact with the present one.

[3] Schake, " Le geometrie degli elementi lineari etc.," *Atii Congr. Bologna*, **4**, 45–50. *Vide* also Beck, "Uber die Lieschen Abbildungen der Linienelemente auf Raumpunkte, " *Math. Zeit.*, Bd. 42.

[4] E. A. Weiss, "Die orientierten Linienelemente einer Kugel als dreifach binares Gebeit," *Deutsche Mathematik*, Jahrg. 3.

and then transferred to a semi-metric 3-space by projection from a generating line. Concurrent line elements are represented by the lines of an elliptic congruence, while circles and turbines correspond to conics. It is found that the transformation group in this representative space is Cubo-cubic. In the last paragraph, it is shown that the analogue to line-element geometry on the Mobius plane is the geometry of " rods " (point pairs at a constant distance apart) under the group of G_k inversions.

2. The invariant concepts of Sphere-Geometry enable us to associate with each prime element in a Euclidean S_n a pencil of spheres in mutual contact and *vice versa*. By means of the representations discussed in T.G. I § 4, these spheres are represented by the points of a tangent line to a quadric Ω in a projective S_{n+1}, or of a generator of a quadric $\overline{\Omega}$ in S_{n+2} according as the elements and hence also the spheres are not, or are oriented.

Thus

> The transformations of prime elements in the extended point transformation of Mobius Geometry (Inversive Geometry) in a Euclidean S_n are isomorphic with the transformations of tangent lines to a fixed quadric in a projective S_{n+1} under the automorphic group of the quadric. Hence the inversive geometry of prime elements in a Mobius S_n is essentially identical in structure with the geometry of isotropic lines in a non-Euclidean S_{n+1}. (2·1)

Similarly

> The geometry of oriented prime elements in a Euclidean S_n under the Lie Group of Sphere transformations is essentially identical with the geometry of generating lines of a quadric variety in a projective S_{n+2} under the automorphic group of the quadric. (2·2)

The generators of a quadric $\overline{\Omega}$ in S_{n+2} may be projected into the tangent lines of a quadric Ω in S_{n+1} by means of a vertex of projection not on $\overline{\Omega}$. We thus establish a (2, 1) correspondence between oriented and non-oriented prime elements, which may be identified with the two single orientations of a doubly oriented [hence non-oriented by T.G. I (1·1)] prime element, if we take for vertex, of projection the point m which is mentioned in T.G. I (3·4) and (4·7).

Two-dimensional circle geometry is somewhat peculiar in that the turbine splits up into two semi-turbines according to my terminology (Kasner's " Turbines "), and requires a separate treatment. In this paper we deal with two-dimensional Mobius Geometry as a geometry of non-oriented line elements.

3. *The Structure of* V_3^4

We have seen that every non-oriented line element in the inversive plane ω (the plane of Mobius Geometry) may be represented by a tangent line to a quadric Ω in S_3. This is equivalent to the transfer of each line element from the plane ω to the sphere Ω by stereographic projection. Again, the lines of a projective S_3 may be represented by points on a Plücker quadric Σ in S_5, the tangent lines Ω being given by the intersection V_3^4 of Σ with another quadric Σ' the special quadratic complex of tangents to Ω. Since each of these representations is free from singular elements, we see that

> the line elements on the Mobius plane may be represented in a (1, 1) manner by the points of a V_3^4 in S_5. The inversive group of the plane induces projective transformations in S_5 which carry the above variety into itself. (3·1)

The lines of the two regulii on the sphere Ω correspond to points on two conics Γ_1, Γ_2 whose planes are conjugate with respect to Σ. Since every tangent to Ω belongs to a pencil formed by two generators one from each regulus, the variety V_3^4 is traced by the lines joining in every way the points on the two conics. The points on each of these "generating lines" (lines in S_5 intersecting Γ_1, and Γ_2) correspond to line-elements through the same point which form what may be called a "star".

The quadric Σ has two systems of generating planes which correspond to lines in the same plane and to lines through a common point in S_3. The sections of Σ' by these two systems of planes[5] give us two systems of conics on V_3^4 whose points correspond respectively to line elements of the same circle, and these line elements turned each through one right angle (a $\pi/2$ turbine). From the known relations between the points in a plane and circles or $\frac{\pi}{2}$ turbines, we infer the following properties of the two systems of "generating conics" of V_3^4. The first of them, for example, follows from the fact that two circles have only two points in common, and hence have common line elements with only two stars.

> Two conics belonging to the same or to different systems are met in general by two generating lines. (3·2)

> Three generating lines are met by one conic of the first system and by one conic of the second system. (3·3)

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[5] Σ is well defined but not Σ' which may be any number of the pencil $\Sigma + k\,\Sigma'$. However, all these cut a generating plane of Σ in the same conic section.

The totality of all generating conics of either system passing through a given point P on V_3^4 generate the same quartic variety P_2^4, called the *turbinoid*[6] *of P*. The surface P_2^4 contains also the generator through P and is formed by the section of V_3^4 by the tangent prime to Σ at P. (3·4)

The points on the turbinoid correspond to the totality of all line elements on the Mobius plane which are concyclic with a given line element, namely the one represented by P. The corresponding tangent lines to Ω meet a fixed tangent line to Ω and thus belong to a special linear complex, whence the result (3·4).

More generally, the tangent lines of Ω which belong to any linear complex, correspond to a prime section of V_3^4. This section contains four generating lines corresponding to four stars at the vertices of a twisted quadrilateral of complex lines lying on Ω. All the four stars coincide in the case of a turbinoid.

If all the line elements of a circle on the sphere Ω be turned in the same sense through the same angle θ, we get a non-oriented semi-turbine. For brevity we shall refer to such a configuration as a θ-turbine. Since the tangents of the sphere corresponding to such line elements belong to a regulus, the representative points in S_5 lie on a conic. The line elements of the turbine associated with the same circle but with the angle $-\theta$ form lines of the complementary regulus, and correspond to a conic on another plane in S_5, the two planes being conjugate with respect to Σ. By varying θ but keeping the circle fixed we get an outer pencil of semi-turbines which are incident with the same " stars ". Interpreting this and the constancy of the angle we see that

there are ∞^4 generating conics on V_3^4 whose planes are the generating planes of the ∞^1 quadrics of the system $\Sigma + k\,\Sigma'$, and these correspond to the θ-turbines (including circles which are 0-turbines) on the Mobius plane ω. An outer pencil of turbines (obtained by varying θ) correspond to conics which meet the same set of generators. Any two of these conics along with Γ_1 and Γ_2 determine on each generator which they all meet, ranges which have the same cross ratio. (3·5)

It is to be noted that the planes of the four conics like those mentioned above are not in general position since there are only 3 lines which meet four arbitrary planes in S_5.[7] It is not difficult to verify that

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[6] The use of the word " turbinoid " in this sense is due to Dr. Weiss.

[7] R. Vaidyanathaswamy, " On the number of lines which meet 4 regions in hyperspace," *Proc. Camb. Phil. Soc.*, **22**, p. 51.

The sections of V_3^4 by the ∞^3 generating planes of the same system of a particular quadric $\Sigma + k\Sigma'$ correspond to the totality of turbines with the same angle θ. The sections by the generating planes of the other system of the same quadric represent turbines whose angle is

$$\theta + \frac{\pi}{2}. \qquad (3\cdot6)$$

Besides generating lines and conics, the variety V_3^4 contains ∞^6 twisted cubics each of which is its residual section with any S_3 passing through a generating line. We shall call the corresponding system of line elements on the Mobius plane ω a *cubic series*. These are the contact elements determined by pairs of circles belonging one to each of two coaxal system, one of the limiting points of one system coinciding with one of the fixed points of the other, so that a star separates out as part of the locus. If this common point be identified with the " point circle at infinity " of the Mobius plane, we see that

A set of line elements whose points lie on a circle and whose lines pass when produced through a fixed point on the circle constitute a cubic series. The general cubic series may be obtained from such particular cases by the operations of the inversive group. (3·7)

A cubic series of the particular type mentioned above (which is the residual locus of a star at ∞ on ω) is defined by a circle with a point marked out on its circumference. The circle is then said to be " cut " at that point. Hence the cubic series defined by a " cut circle " consists of line elements whose points lie on the circle and which are directed towards the point where it is cut.

4. *Projection of* V_3^4 *on a 3- space R*

We now project the V_3^4 on a 3-space R taking as the region of vertices a generating line cutting the conics Γ_1 and Γ_2 at, say, J_1 and J_2 respectively, and thus obtain a representation of the line-elements of ω by points in R. A plane (two-space) containing the line $J_1 J_2$ meets V_3^4 in 4 points of which 3 are absorbed by $J_1 J_2$ and one point Q stands out distinct. If the same plane meets R in a point q, we regard q as the projection of Q.

The conics Γ_1 and Γ_2 project into two lines γ_1 and γ_2 which are thus in projective correspondence with the two conics. To the points J_1 and J_2 thus correspond two points j_1 and j_2 which are the intersections of γ_1 and γ_2 with the planes through $J_1 J_2$ and tangents to the conics at J_1 and J_2. A generating line meeting Γ_1 and Γ_2 at P_1 and P_2 projects into a line meeting γ_1, γ_2 at p_1, p_2. When P_1 and P_2 tend to J_1 and J_2, the projection approaches $j_1 j_2$ as a limit. However, the correspondence between the points on $J_1 J_2$

and $j_1 j_2$ will depend on the manner of approach of P_1 and P_2 so that all we can assert is that

the projection of a point J on $J_1 J_2$ is a point j on $j_1 j_2$ whose position depends on the manner in which J is approached. (4·1)

The (1, 1) character of the correspondence between V_3^4 and R breaks down also for points on γ_1 and γ_2. For if p_1 on γ_1 be the projection of P_1 on Γ_1, the plane $J_1 J_2 p_1$ cuts V_3^4 in $J_1 J_2$ and in the line $J_2 P_1$.

Thus

Any point p_1 on γ_1 is the projection not only of a point P_1 on Γ_1 but also of all points on the line $J_2 P_1$. Similarly any point p_2 on γ_2 is the projection of all points on a line $J_1 P_2$. (4·2)

The ∞^4 generating conics of V_3^4 project into ∞^4 conics in R. Now each conic determines a (1, 1) correspondence between Γ_1 and Γ_2 by means of the generating lines which meet all the three conics. Let J_1, J_2 correspond to P_2 and P_1 in this correspondence. In R we have now a (1, 1) correspondence between γ_1 and γ_2 and hence the joins generate a quadric regulus containing, in particular, the lines $j_1 p_2$ and $j_2 p_1$. Also since the conic in S_5 meets $J_1 P_2$ and $J_2 P_1$, its projection in R passes through p_2 and p_1 by (4·2). Thus $j_1 p_1 = \gamma_1$, $j_2 p_2 = \gamma_2$, $j_1 p_2$, and $j_2 p_1$ form a twisted quadrilateral on the quadric, so that $p_1 p_2$ is the polar line of $j_1 j_2$. The conic in R is thus a section of the quadric by a plane through $p_1 p_2$, that is, by the polar plane of a point on $j_1 j_2$.

Hence

The ∞^4 generating conics of V_3^4 representing the turbines (and in particular, the circles) of ω project into ∞^4 conics which are the sections of ∞^3 quadrics through γ_1, γ_2 by their polar planes w. r. t. the ∞^1 points on $j_1 j_2$. (4·3)

Now the points or stars, associated with the line elements of a turbine correspond to the generators of the quadric, and they are the same for all turbines of an outer pencil.

Hence

The section of the same quadric through γ_1, γ_2 by the polar planes of different points on $j_1 j_2$ correspond to an outer pencil of turbines. (4·4)

Complementary to the above is the following result which we shall presently establish :

The section of different quadrics through γ_1, γ_2 by their polar planes w.r.t. the same point j (θ) on $j_1 j_2$ are turbines with the same angle θ.

Hence

The planes of all such conics cut $j_1\ j_2$ at a fixed point $j'\ (\theta)$ the harmonic conjugate of $j\ (\theta)$ w.r.t. j_1 and j_2. (4·5)

A turbine is determined by its outer circle and the angel θ ; we thus have the striking result that the quadric determines the former and the plane of section, the latter.

A star is a turbine whose outer circle is of zero radius, and whose angle θ is indeterminate. Hence among the system of generating planes of $\Sigma + k\Sigma'$ where $k = k\ (\theta)$ all of which cut V_3^4 in θ turbines [*vide* (3·6)], there will be one through each generating line of V_3^4. These planes have the property that all their 4 intersections with V_3^4 are absorbed by the generating line through which they pass, unlike other planes which have one residual intersection. For, the 4 intersections of a general plane in S_5 with V_3^4 represent the 4 generators of an arbitrary regulus which touch the sphere Ω. When the regulus degenerates into two plane pencils, one of which is a tangent pencil to Ω at say A, and the other has vertex B, the plane in S_5 passes through a generator corresponding to the star at A, and the residual intersection represents the tangent in the pencil with vertex B other than BA. Now the line elements of a turbine on Ω define a regulus of a quadric having ring contact with Ω and so a turbine will contain a star only when this ring contact quadric breaks up into two planes. But in such a case the planes are coincident and a residual line not belonging to the star does not exist. Hence the property stated above.

Let p be an arbitrary generating plane of $\Sigma + k\,\Sigma'$ of that system whose section by V_3^4 gives θ turbines, and p_j the particular generating plane which passes through $J_1\ J_2$. Since p_j has no residual intersection with V_3^4 outside $J_1\ J_2$ it follows by (4·1) that it meets $j_1\ j_2$ in a point $j'\ (\theta)$. Also p and p_j meet since they are generating planes of the same system of a quadric in S_5, and the projection of this point is j' since all points on p_j project into j'. It follows, therefore, that the projecion of p is a plane through $j'\ (\theta)$ which proves (4·5).

The range of points $j\ (\theta)$ or $j'\ (\theta)$ are in projective correspondence with the quadrics $\Sigma + k\,\Sigma'$. The points j_1 and j_2 correspond to the turbines formed by the generators of Ω, *i.e.*, the turbines whose ring contact quadric coincides with Ω.

I shall use the word " T-conics " to denote those conics in the representative 3-space R which correspond to turbines on the sphere Ω or the inversive plane ω. The particular T-conics which represent circles will be called " C-conics ".

On any particular plane in R there are ∞^1 T-conics which have double contact with one another at the points where the plane meets γ_1 and γ_2. The pole of this chord of contact lies on $j_1\, j_2$. (4·6)

For, if the plane meets $j_1\, j_2$ in j', these conics are by (4·3) the sections of quadrics through γ_1, γ_2 by their polar planes w. r. t. j, the harmonic conjugate of j' w.r.t. j_1 and j_2.

For using the notation of (4·5), if the given plane cuts γ_1, γ_2 in p_1, p_2 it will be the polar plane of the point j only when the quadric passes through $j_1\, p_2$ and $j_2\, p_1$, in addition to $j_1\, p_1 = \gamma_1$ and $j_2\, p_2 = \gamma_2$. The pole of $p_1\, p_2$ for all such sections is j'.

5. By selecting a particular generator $J_1\, J_2$ as the axis of projection we have singled out a particular point J on Ω and hence also a point on ω for special notice. We identify this with the " point circle at infinity " of the Mobius plane.

A straight line in general position in R is the projecion of the section of V_3^4 by a 3-space through the line and $J_1\, J_2$, *i.e.*, of a twisted cubic which is the residual of a " star at infinity ".

Hence

A straight line in general position in R corresponds to the line elements of a cut circle. If the line meets $j_1\, j_2$, at j' (θ) the line elements cut a straight line at a constant angle θ. (5·1)

We have already seen that any quadric through $\gamma_1\, \gamma_2$ defines a circle on ω. (5·1) enables us to interpret the two systems of generating lines of such a quadric.

One system of generating lines of a quadric surface through γ_1 and γ_2 correspond to stars incident with a particular circle. The other system of lines represent cubic series obtained by the same circle cut at any of its points. (5·2)

Again consider a conic in R which represents the line elements of a circle on ω. The plane of this C-conic passes through j' (0). The line joining any two points on the conic corresponds to the line elements of a cubic series in ω determined by any two line elements of the circle. They belong to a cut circle passing through the centre C of the given circle and cut at the diametrically opposite point. The line element at any point P will be found to be perpendicular to CP. By forming all cubic series by combining pairs of elements of the circle, we get all line elements corresponding to points on the plane.

Hence

The line elements on ω corresponding to points on a plane in R meeting $j_1\, j_2$ in j' (0), belong to a system of concentric circles. The

conics of (4·6) correspond to the several circles, and the congruence line $p_1\ p_2$ to the star at the common centre. (5·3)

It can be similarly proved that

If all the line elements of a system of concentric circles on be turned through the same angle θ they correspond to points on a plane cutting $j_1\ j_2$ in j' (6). (5·4)

If, however, a plane in R passes through $j_1\ j_2$, it is the section of R by the turbinoid of a point on $J_1\ J_2$. On Ω it represents line elements concyclic with a particular line element through the " point at infinity ".

Hence,

A plane through $j_1\ j_2$ represents a field of parallel line elements. In particular, the planes through $j_1\ j_2\ \gamma_1$ and $j_1\ j_2\ \gamma_2$ corresponding to isotropic line elements. (5·5)

6. *Real Representations in a Semi Metric R*

We may, without loss of generality, choose a system of homogeneous co-ordinates ξ_r $(r = 0, 1, 2, \cdots 6)$ in S_5 so that points on the conic Γ_1 (corresponding to one system of generators of Ω) may be represented by $(\rho_1\lambda^2,\ \rho_1\lambda,\ \rho_1,\ 0,\ 0,\ 0)$ and points on the conic Γ_2 corresponding to the other system by $(0,\ 0,\ 0,\ \rho_2,\ \rho_2\mu,\ \rho_2\mu^2)$. The quadrics $\Sigma + k\ \Sigma'$ are thus given by $k_1\ (\xi_0\xi_2 - \xi_1^2) + k_2\ (\xi_3\ \xi_5 - \xi_4^2) = 0$, and we may identify Σ with the quadric $k_1 = k_2$, Σ' corresponding to an unspecified member of the system.

Any line element on Ω through the point $(\lambda,\ \mu)$ is specified by the ratio $d\lambda/d\mu$. Hence the variety V_3^4 is given by $(\rho_1\lambda^2 d\ \mu,\ \rho_1\lambda d\ \mu,\ \rho_1 d\ \mu,\ \rho_2 d\lambda,\ \rho_2\mu\ d\lambda,\ \rho_2\mu^2 d\ \lambda)$. On every generating line the points corresponding to the values 0 and ∞ for $d\lambda/d\mu$ are known. The projective metric on the line will be completely fixed by giving say, the point for which $d\lambda/d\mu = 1$. We take this to be the point where the prime $\xi_2 = \xi_3$ cuts it, so that we have $\rho_1 = \rho_2$. This is equivalent to taking a parallel field of elements on ω, the turbinoid of the point $(1,\ 0,\ 0,\ 0,\ 0,\ -1)$.

The points on Γ_1 and Γ_2 corresponding to infinite values of the generator co-ordinates λ and μ are $(1,\ 0,\ 0,\ 0,\ 0,\ 0)$ and $(0,\ 0,\ 0,\ 0,\ 0,\ 1)$ and these we identify with J_1 and J_2. We project the point on V_3^4

$$(\xi_0,\ \xi_1,\ \xi_2,\ \xi_3,\ \xi_4,\ \xi_5) = (\lambda^2 d\mu,\ \lambda d\mu,\ d\mu,\ d\lambda,\ \mu d\lambda,\ \mu^2 d\lambda) \qquad (6\cdot1)$$

from $J_1\ J_2$ as axis on the 3-space $\xi_0 = 0$, $\xi_5 = 0$ which we identify with R, and obtain the point

$$(\xi_1,\ \xi_2,\ \xi_3,\ \xi_4) = (\lambda d\mu,\ d\mu,\ d\lambda,\ \mu d\lambda) \qquad (6\cdot2)$$

and these we take to be the homogeneous co-ordinates of the representative point in R. We may identify the generator co-ordinates λ, μ on Ω with the

isotropic co-ordinates $y - ix$ and $y + ix$ on ω thus converting the latter into a double binary domain. To get a representation of real line elements by real points in R, we perform a transformation of co-ordinates from ξ_r to X_r thus getting

$$\left.\begin{aligned} X_1 &= (\xi_1 + \xi_4)/2 = (\lambda d\mu + \mu d\lambda)/2 = x\,dx + y\,dy \\ X_2 &= (\xi_1 - \xi_4)/2i = (\lambda d\mu - \mu d\lambda)/2i = y dx - x dy \\ X_3 &= (\xi_2 + \xi_3)/2 = (d\mu + d\lambda)/2 = dy \\ X_4 &= (\xi_2 - \xi_3)/2i = (d\mu - d\lambda)/2i = dx \end{aligned}\right\} \qquad (6\cdot3)$$

as the homogeneous co-ordinates of the line element determined by the point (x, y) and the direction dy/dx on the Cartesian plane.

If we prefer to use non-homogeneous co-ordinates we may take

$$X = x + yp,\ Y = y - xp,\ Z = p, \text{ where } p = dy/dx. \qquad (6\cdot4)$$

These give

$$x = \frac{X - YZ}{1 + Z^2};\ y = \frac{XZ + Y}{1 + Z^2};\ p = Z. \qquad (6\cdot5)$$

The points j_1, j_2 are found to be given by $(X_1, X_2, X_3, X_4) = (1, -i, 0, 0)$ and $(1, i, 0, 0)$ respectively so that $j_1 j_2$ is the line $X_3 = X_4 = 0$ (the " line at infinity " on $Z = 0$). The lines γ_1, γ_2 are given by $X_2 + i X_1 = 0$, $X_3 - iX_4 = 0$, and $X_2 - iX_1 = 0$, $X_3 + iX_4 = 0$; or by $Y = \mp iX$, $Z = \pm i$.

We have in R three significant lines $j_1 j_2$, γ_1, γ_2. We take the first of these as a " line at infinity " and j_1 and j_2 as the absolute points on it. Thus any plane $Z = \text{const.}$ is Euclidean. However, the choice of $X_4 = 0$ as the " plane at infinity " in the X, Y, Z co-ordinates (6·4) is arbitrary, and there is no Absolute conic in this plane, unless we select a particular quadric through γ_1, γ_2 and hence also a particular circle on ω for special notice. Thus our space is semi-metric in the sense that metrical ideas apply only to the planes $Z = \text{constant}$.

It will be shown later that the inversive group of ω induces a cubo-cubic Cremona space transformation of R into itself so that projective concepts in R have no invariant significance. However, since the two systems of generating lines on Ω are transformed into themselves or into each other, it follows that

> The inversive group of ω induces projective transformations of γ_1 γ_2 into themselves or each into the other. Any transversal of γ_1 γ_2 is transformed into another transversal, and the two are in projective correspondence. (6·6)

The last statement merely expresses that stars are inverted into stars. Other straight lines in R will, in general, be transformed into twisted cubics.

The equations (6·3) and (6·4) enable us to verify the truths of the results already proved. Thus the line elements of the concentric system of circles given by $(x-a)+(y-b)\,p=0$ are represented by points on $X-bZ-a=0$, a plane parallel to the Y-axis. Hence the point at infinity on the Y-axis (which we shall denote by Y_∞) is the point j' (0), and the point at infinity on the X-axis (X_∞) is j (0). A line through j (0) is given by $Y=c$, $Z=m$, *i.e.*, by $y=xm+c$, $p=m$ which are the line elements of a straight line. Equations (5·4) show that the line of the congruence corresponding to the star at (x, y) is given by

$$\frac{X-x}{y}=\frac{Y-y}{-x}=Z$$

which cuts $Z=0$ in $(x, y, 0)$.

Hence,

Let us identify the plane ω with $Z=0$ representing a point on it by (a, b) or $(a, b, 0)$ according as we conceive of it as belonging to the former or the latter. The star at any point P (x, y) is then represented by the congruence line through P $(x, y, 0)$. A particular line element is located by the additional relation $Z=p$. (6·7)

The spatial co-ordinates of a line element may be obtained geometrically thus: its X co-ordinate is the intercept of the normal to the element on the X-axis, its Y-co-ordinate is the intercept which the line of the element makes on the Y-axis, and its Z is p.

7. *The Hart-Circle and Miquel-Clifford Configurations in Line Element Geometry*

The considerations of the preceding paragraphs provide us with a principle of transference by which any configuration in the inversive plane may be associated with a corresponding configuration in R. It is only necessary to remember that to a point corresponds a "congruence line" meeting γ_1 and γ_2, the angle between two line elements corresponding to the "separation" of the two points with reference to the intersections with γ_1 and γ_2 as absolute points. Also that to a circle corresponds a C-conic and that

a C-conic is one which meets γ_1 and γ_2 and has its tangents at these points parallel to the Y-axis. (7·1)

If we apply the Principle of Transference to a Hart System we have the result:—

It is possible to find in R two tetrads of C-conics such that every conic of one tetrad intersects all the conics of the other tetrad.

In the same manner, the Miquel-Clifford Configuration regarded as one in the inversive plane gives rise to the following:

For every positive integral value of n it is possible to find systems of 2^n C-conics and 2^n congruence lines with the property

(i) every congruence line is met by exactly $n+1$ C-conics;

(ii) every conic is met by exactly $n+1$ congruence lines; also,

(iii) the range of points determined on any congruence line by the conics which meet it, is projective with the range on any other congruence line.[8] (7·2)

8. *The Cubo-Cubic Transformations in R induced by the Inversive Group on the Plane*

The effect of inversion with respect to a given circle is to replace every star on ω by a star at the inverse point. Corresponding line elements are those which lie on the same circle. Hence the effect of the inversion on R is firstly to replace a congruence line by another congruence line, such that their intersections with $Z = 0$ are inverse points. A C-conic which meets both the congruence lines cuts out corresponding points on them.

Let us examine how planes in R are transformed. A plane in R is the projection from $J_1\ J_2$ of the section of V_3^4 by the 4-space through the plane and J_1 and J_2. Since inversion is equivalent to a projective transformation of V_3^4 into itself, the section is carried over into another section of V_3^4 by a 4-space through another generator $Q_1\ Q_2$. This section is a V_2^4 which meets all generators and, in particular, $J_1\ J_2$. Hence its projection from $J_1\ J_2$—the transform of the original plane—is a cubic surface through $q_1\ q_2$. This last line represents the transform of the star at the "point at infinity" *i.e.*, the star at the centre of inversion. If the centre of inversion be (0, 0) the line $q_1\ q_2$ is the Z axis.

Geometrical considerations lead to the conclusion that the cubic surfaces pass through the lines γ_1, γ_2. For, equations (6·4) show that all line elements of the same isotropic line on the projective plane ω correspond to the same point in R, while line elements of different isotropic lines correspond to the several points on γ_1 or γ_2. Now, among the line elements of a concentric system of circles there are only two which are isotropic, since all such circles touch at the circular points. These two correspond, in fact, to the two intersections of the representative plane in R with γ_1 and γ_2. On inversion, we get the line elements of a co-axial system of circles and these include line elements belonging to all the isotropic lines in the plane. Hence the result. We shall

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[8] *Vide* "The Miquel-Clifford Configuration in the Geometries of Mobius and Lagurre", *Annamalai Univ. Jour.*, **7**, 6–12.

see later that the cubic surfaces touch along γ_1 and γ_2 so that these count each as two lines.[9]

A line in R is the projection of a section of V_3^4 by the 3-space through it and $J_1 J_2$, that is of a twisted cubic on V_3^4 meeting $J_1 J_2$ twice. This is carried over into another twisted cubic which meets $Q_1 Q_2$—the transform of $J_1 J_2$—but which will not, in general meet, $J_1 J_2$. Hence a straight line transforms into a twisted cubic meeting $q_1 q_2$. The transformations of R induced by the inversive group of ω is thus cubo-cubic.

Analytically, the effect of inversion in say, $x^2 + y^2 = k^2$ is to replace the line element x, y, p by $k^2 x/(x^2 + y^2)$, $k^2 y/(x^2 + y^2)$, p'

where
$$p' = \frac{(x^2 + y^2)\, p - 2y\,(x + yp)}{(x^2 + y^2) - 2x\,(x + yp)}.$$

Hence if X_1', X_2', X_3', X_4' are the co-ordinates of the transform of $X_1\ X_2\ X_3\ X_4$, we have,

$$\left.\begin{aligned} \rho\, X_1' &= k^2 X_1 (X_3^2 + X_4^2) \\ \rho\, X_2' &= -k^2 X_2 (X_3^2 + X_4^2) \\ \rho\, X_3' &= [(X_1^2 - X_2^2) X_3 + 2X_1 X_2 X_4] \\ \rho\, X_4' &= X_1^2 - X_2^2 - 2X_1 X_2 X_3. \end{aligned}\right\} \qquad (8\cdot 1)$$

It will be found that the homoloidal family of cubic surfaces pass through the lines $X_1 = X_2 = 0$ and through $X_3 = X_4 = 0$ and touch the planes $X_3 = \pm i X_4$ along the lines γ_2 and γ_1 respectively. The F-element is thus a sextic curve which breaks up into 6 lines, of which two coincide with γ_1 and two with γ_2. The four points where these lines meet are obviously singular points for the cubic surfaces.

The equations of transformation take a simpler form when referred to the imaginary co-ordinates

$$\xi_1' : \xi_2' : \xi_3' : \xi_4' = k^2\, \xi_2\, \xi_3\, \xi_4 : \xi_1\, \xi_4^2 : \xi_1^2\, \xi_4 : k^2\, \xi_1\, \xi_2\, \xi_3 \qquad (8\cdot 2)$$

A pair of points in R have an absolute invariant under the Cremona Group, and hence there is a sort of a metric though not of the usual type. For two points on the same congruence line, it is the " separation " mentioned in the beginning of Para 6 and corresponds to the angle between the line elements of the same star. If the points are not on the same congruence line, the invariant in question is the " separation " of either point from the intersection of the turbinoid of the other with the congruence line through it. On ω it is the angle between either line element and the circle through its point and the other line element. It may also be interpreted as twice

[9] A line along which the surfaces of a homoloidal web touch a plane counts as two F-lines. *Vide* Hudson, *Cremona Transformations* (1927), p. 248.

the angle of the unique turbine which contains both the line elements. It will be obvious that

(i) the locus of line elements on ω with a zero " separation " from a given line element is the totality of elements concyclic with it—the turbinoid of that element ;

(ii) while the " separation " of line elements of different stars is unique even when approached as a limit, the " separation " of elements of the same star becomes indeterminate as a limit.

9. *Analogous Results in the Geometry G_k*

In my paper (T.G. II), I have worked out the details of a generalisation of Mobius Geometry in which non-oriented circles of a fixed radius k (called k-circles) play the same role as do point circles in the former. The totality of k-circles may be represented by points on a quadric Ω' which touches Ω at its point at infinity J. By stereographic projection from J we may establish a one-one correspondence between the Mobius plane ω and the plane ω' of G_k geometry (supposed superposed) in which each point P on ω corresponds to the circle with centre P and radius k on ω'. To a line element of ω correspond two neighbouring k-circles and these cut in 2 points at a constant distance $2k$. We shall refer to such a configuration of two points as a " rod ". Thus

> In the correspondence between Mobius- and G_k-geometries, a line element of the former corresponds to a " rod " perpendicular to the element and whose centre coincides with the point of the element. (9·1)

Just as tangent lines to Ω define line elements by means of co-axal systems of circles which all touch, so also a tangent line to Ω' defines a rod by means of a co-axal system of circles whose common points are the extremities of the rod. Thus rod-geometry in G_k is isomorphic with the geometry of tangent lines to Ω' under the projective group. We may thus reinterpret all our results taking V_3^4 as the representative space of line elements on Ω' instead of on Ω. I shall content myself with giving only the results, since they follow readily from the results already established in this paper and the results in T.G. II.

No.	Representative 3-space with an invariant quadric Q (Ω or Ω')	Mobius Plane	G_k Plane
1	Point P on Q	Point circle P	k-circle P
2	Point on tangent plane at P	Proper circle ($r \neq 0$) through P	Proper circle ($r \neq k$) bisecting P
3	Line element on Q	Line element	" Rod "
4	Angle between line elements of the same star (invariant)	Angle between line elements at a point (invariant)	Angle between two rods with the same centre (invariant)
5	Corresponding tangents in an automorphic involution of Q meet	A line element and its inverse are concyclic	The extremities of a rod and its G_k inverse are concyclic
6	Turbine on Q	Turbine	Rods with centres on a circle and cutting it at a constant angle
7	Line elements belonging to a linear complex	Line elements of a co-axal system of circles	Rods touching the circles of the orthogonal co-axal system at their middle points
8	Special linear complex of lines meeting a given tangent line	Turbinoid of a given element	Rods whose extremities are concyclic with those of a given rod

In conclusion it may be added that by fixing the order in which the two points which define a rod are to be taken we have a geometry of oriented rods analogous to the geometry of oriented line elements on a plane or sphere.

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